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# THE CHEMISTRY OF HIGH POLYMERS

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*By*
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UNIVERSITY OF BRISTOL

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# PREFACE

THIS book is addressed to the reader who wishes to become familiar with some of the basic ideas of the physics and chemistry of high polymers. The text is based on a series of postgraduate lectures given in the University of Bristol in the autumn of 1946 to graduate chemistry students and industrial chemists. The original lecture notes have been expanded and are presented in a form suitable for students entering the field of high polymer research and for those engaged in industry who desire to know more about the fundamental advances in this new and rapidly developing subject. It is hoped that the book will also be of service to chemists already acquainted with this subject.

Polymer chemistry is a very large subject and one which is growing rapidly. It encompasses the wide field of natural products such as rubber, proteins, cellulose and other polysaccharides, together with the large group of synthetic substances formed by established chemical processes. It is obvious that a detailed and comprehensive treatment of these subjects would be beyond the scope of a single contributor. Many excellent treatises are already available on the special classes of polymers, but these books are on the whole unsuitable for the beginner or non-specialist. Certain general principles must, of course, be of common applicability to all macromolecules whatever their nature, and it is primarily with these fundamentals that this introductory account is concerned. An attempt has been made to explain these basic ideas as simply as possible, and to this end extensive use has been made of graphical and pictorial representations.

The development of the subject matter proceeds from an introductory account of the nature and structure of high polymeric molecules to that of the interesting problem of the mechanism of formation of the different types of polymer. Since the properties of large molecules are intimately linked with their size and shape, these subjects are treated in some detail in subsequent chapters. From the point of view of the technical application of high polymers, the solid state is of major interest and importance. The latter part of this book is devoted to this topic and deals with the nature and structure of solid polymers, together with a survey of the present state of our knowledge regarding the relationship between molecular structure and arrangement, and solid properties.

Reference in the text to the literature is limited; an attempt has been made to give the more general references or those which will provide the reader with a convenient key to further information. In writing the book the author has made use of many of the general and specialized treatises on the subject and to the authors of these works he expresses his indebtedness. These general references are summarized at the end of Chapter 1 and the reader is referred to them for further information.

The author wishes to express his deep appreciation to Mr. R. F. J. FREEMAN, Dr. C. F. H. TIPPER and Mr. F. J. WHITBY, who assisted in reading the manuscript and in the correction of proofs, and to Dr. A. M. KING for her generous help in the preparation of the manuscript. Finally, thanks are due to Mr. D. R. REXWORTHY, of Messrs. Butterworths Scientific Publications, for his helpful cooperation during the publication of this volume.

*February* 1948 C. E. H. BAWN

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*Journal of Applied Physics* *Figure 57.*
*Journal of Chemical Physics* *Figure 29.*

The author is indebted to Professor W. T. ASTBURY for the X-ray photographs shown in *Plate 1.*

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# CHAPTER 1

# INTRODUCTION

# NATURE AND TYPES OF POLYMER

THE BASIC PRINCIPLES underlying the formation and the structure of synthetic polymers are now clear. Systematic and extensive investigations, mainly during the last twenty years, have elucidated the nature of the polymerization process, the types of molecule which give rise to macromolecules, and the dependence of the processes on the arrangement of atomic molecular groups in the reacting molecules. These discoveries constitute one of the major advances in modern chemistry. But while the general chemical principles are clear and the more important groups of polymers have been recognized, much remains to be done in completing and systematizing the large mass of experimental data, and in understanding the detailed mechanism of the polymerization process.

The most remarkable feature of high polymers, and the one which differentiates them from other types of organic molecule, is their mechanical properties—their tensile strength, elasticity, deformability, and hardness. These properties are intimately connected with the structure and configuration of the polymer molecule, and the ultimate aim of investigations in this field is the direct correlation of structure with the properties of the solid, in the hope that one day it may be possible to predict the nature and properties of a polymer from a knowledge of the composition and configuration of its monomer.

Although most of the topics discussed in the subsequent chapters are related to synthetic polymers, it must be emphasized that by far the largest groups of high polymers are the natural products—proteins, starch, cellulose, rubber, *etc*—which constitute the basis and the tissue of life. Each of these subjects would require a separate study, and their detailed treatment would be beyond the scope of the present work.

## NATURE OF THE POLYMER MOLECULE

The simplest type of polymer structure consists of a large number of groups of atoms (structural units) joined together by homopolar bonds in the form of a chain. We may, in conformity with the usual chemical nomenclature, refer to such a chain as a molecule. Unlike simple organic substances, however, synthetic high polymers do not consist of an assembly of molecules of identical dimensions, but are composed of mixtures of chains of different lengths. In any laboratory process employed for the production of long chains from a given monomer, the product is not an entirely haphazard collection of chain lengths, but corresponds to a well defined distribution of sizes which is determined by the detailed mechanism of the polymerization reaction.

Besides the distribution in sizes of the linear molecules, variation of composition along the molecule chain may be encountered. For example, the molecule may be formed by polymerizing together two or more monomers to give a product in which the monomers are not arranged in a perfectly orderly manner with uniform distribution along the chains; or, starting with a polymeric mixture of known chain distribution, such as cellulose, partial substitution of the –OH groups to give cellulose derivatives results in non-uniformity of chemical composition within the molecule. In some cases different forms of linkage between similar monomers may exist in the same molecule; for example, butadiene, $\underset{1}{C}H_2{=}\underset{2}{C}H{-}\underset{3}{C}H{=}\underset{4}{C}H_2$, may link up by 1,2 and 1,4 addition, and furthermore we have the stereochemical possibility that some molecules may unite in the *cis* and others in the *trans* positions.

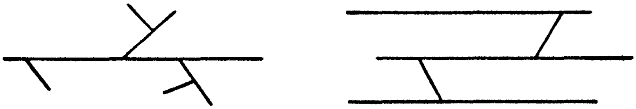


*Figure 1. Diagrammatic representation of* a *chain branching,* b *cross linking of chains*

In addition to the variation in length and composition of molecules in chain polymers, non-linear systems may be formed by branching of the chain (*Figure 1*a) or cross linking between chains (*Figure 1*b), and this introduces an additional variable size factor.

As a rule, therefore, a polymer will be composed of a mixture of molecules of different sizes, and hence of different molecular weights, yet with identical chemical linkages; also, in some cases, there will be a mixture of stereoisomers, together with different degrees of branching and cross linking. In order to define such a polymer completely, chemical composition and distribution of molecular size are not enough—a knowledge of the shape of the molecules is also a necessity.

Experimental methods for the study of these various aspects of the chemistry of high polymers have required the development of special techniques to supplement and extend the familiar methods. The general experimental results may be considered under the following four headings:

*a Chemical Structure*—In many polymerizations the nature of the grouping of the units within the molecule may be foretold from the structure of the monomer from which it is prepared. In general, however, the detailed arrangement of the groups must be determined by the standard methods of organic chemistry and chemical analysis, supplemented by special methods such as x-ray analysis, and ultraviolet and infra-red absorption spectroscopy.

*b Molecular Size and Shape*—Since high polymers cannot be sublimed or vaporized without decomposition, molecular size distribution and molecular shape are determined by investigation of the properties of dilute solutions of the polymer. Properties which depend on the size of the molecules, such as solubility, osmotic properties, and mechanical properties (viscosity), would be expected to exhibit features of interest, and it is from this type of measurement that the configuration of the molecule is deduced.

*c Mechanism and Kinetics of Formation*—A thorough understanding of the chemical reactions leading to the formation of high polymers requires a knowledge of the chemical nature and rates of the different elementary processes occurring. This is the aim of the kinetic analysis of polymerization processes. These results also provide a method for the theoretical calculation of molecular weight distributions.

*d Nature and Properties of the Solid State*—The normal state of the high polymer at ordinary temperatures is the solid, and this is also the state which is most important technically. It is natural, therefore, that particular attention should have been given to the determination of the structural configurations which determine the characteristic mechanical, thermal, and electrical properties, and which give rise, within a class of substances built upon the same fundamental principles, to the states often classified as rubbers, plastics, and fibres.

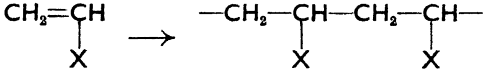
The presentation adopted in the following chapters follows closely the above plan of classification of subject matter. The developments in polymer chemistry during the last few years have, however, been so immense that it would be impossible in any single volume to cover more than a fraction of reported experimental material. The object of this book is, therefore, to present a general, rather than an elaborate or detailed, description of our present day knowledge of polymeric substances from the point of view of their method of study and of the principles and theories which determine their characteristic behaviour.

## CLASSIFICATION OF HIGH POLYMERS

It is generally agreed that, from the chemical viewpoint, polymers can be classified broadly into two types, according to their characteristic modes of formation, *viz*:

1. *Condensation Polymers*, in which the monomers interact by familiar chemical processes involving the elimination of water or other simple molecules ($NH_3$, HCl, or NaCl), the structure of the monomer being such that the process can repeat itself in building up the polymer molecule. Since molecules are lost, the ultimate analysis of the polymer is different from that of the monomer from which it was formed.
2. *Addition Polymers*, in which the monomers unite together without forming any other products. The ultimate analysis of the polymer, (-M-M-M-M-), is identical with that of the monomer (M). When two or more types of monomer are used, the product, known as a copolymer, contains all types of the initial interacting units.

The more important of the addition polymers are formed from unsaturated derivatives of the type $CH_2{=}CHX$. For example,

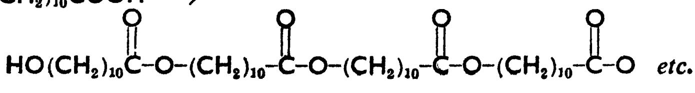


$$\underset{\displaystyle X}{CH_2{=}\underset{|}{C}H} \longrightarrow -CH_2-\underset{\underset{\displaystyle X}{|}}{C}H-CH_2-\underset{\underset{\displaystyle X}{|}}{C}H-$$

These are also commonly known as vinyl polymers, since the majority of polymerizable monomers may be regarded as derivatives of vinyl alcohol, $CH_2{=}CHOH$. Neglecting the end groups—and this is justifiable for a long chain—the molecular formula of the polymer is $(CH_2{-}CHX)_n$.

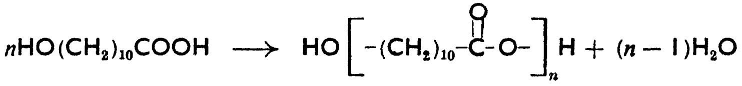
In contrast, condensation polymers are formed from monomers carrying reactive groups which may condense together, with the elimination of a simple molecule, usually water. Chemists are familiar with simple esterification reactions which proceed with the elimination of water, and it is obvious in this case that, for a polyester to be formed, the reacting monomer should possess at least two groups which can take part in a condensation reaction; for example, the self-esterification of a hydroxyacid such as ω-hydroxyundecanoic acid:

$HO(CH_2)_{10}COOH \longrightarrow$



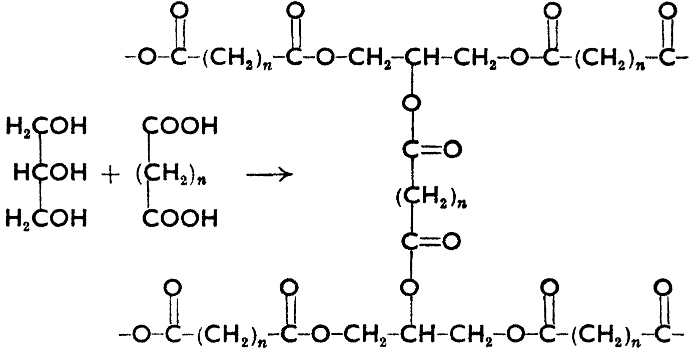
$$HO(CH_2)_{10}\overset{\overset{\displaystyle O}{\|}}{C}-O-(CH_2)_{10}-\overset{\overset{\displaystyle O}{\|}}{C}-O-(CH_2)_{10}-\overset{\overset{\displaystyle O}{\|}}{C}-O-(CH_2)_{10}-\overset{\overset{\displaystyle O}{\|}}{C}-O \quad etc.$$

It is usual to employ an abbreviated formula for the polymer, in which the repeating unit is enclosed in square brackets, the subscript indicating the number of times the unit repeats in the polymer. Thus, for the above example the reaction leading to the $n$-mer is



$$n\mathrm{HO(CH_2)_{10}COOH} \longrightarrow \mathrm{HO}\left[-(\mathrm{CH_2})_{10}-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{O}-\right]_n\mathrm{H} + (n-1)\mathrm{H_2O}$$

It will be seen that the type of reaction is dependent on the number of reactive groups, termed by Carothers *functional groups.*[1] The functionality of a molecule is the number of groups it contains which can react with another molecule leading to bond formation. Bifunctional molecules lead to the formation of long chains, usually referred to as linear molecules. If the monomer is of functionality greater than two, the polymerizing molecule can grow in more than one dimension, giving rise to a giant three-dimensional network. For example,

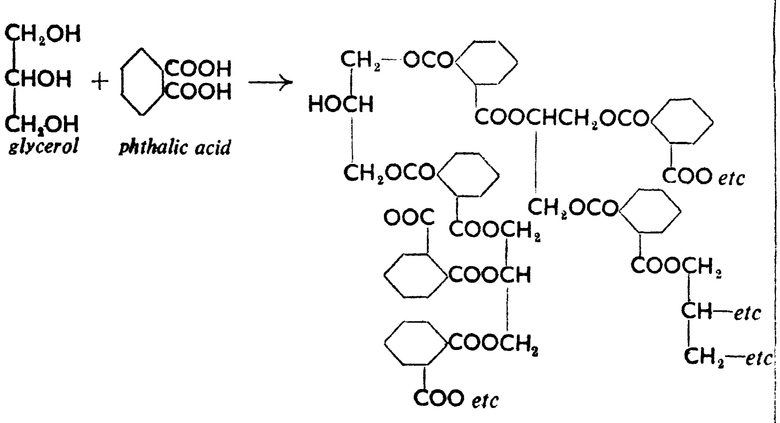


The properties of such molecules differ very markedly from those of the linear polymers, and the two types of structure can be readily differentiated experimentally.

## CONDENSATION POLYMERIZATION

High polymers may be obtained by a wide variety of condensation reactions, the necessary requirement being that the reacting monomer or pair of monomers should carry two or more condensable functional groups. It is not proposed to consider the detailed organic chemistry of these reactions, but it will suffice for the present purpose to summarize the more important reaction types. A list of these reactions, together with some of the characteristic properties of the polymers, is given in *Table I.* The terminology of the polymers, polyesters, polyethers, polyamides, *etc*, is self evident,

## Table I
### Synthetic Condensation Polymers

| Type | Example | Properties |
|---|---|---|
| *Polyester* | $HO{\cdot}(CH_2)_9COOH \longrightarrow HO{-}[(CH\ )_{,}COO]_n{-}H$<br>*ω-hydroxydecanoic acid* | *M.* 780–25,000, *m.p* 66–80°C. *Strong orientated fibres above m.p* 9,300 |
| | $HO{\cdot}(CH_2)_3OH + HOOC(CH_2)_{16}COOH \longrightarrow HO{-}[(CH_2)_3OCO(CH_2)_{16}COO]_x{-}H$<br>*trimethyleneglycol* *hexadecamethylene dicarboxylic acid* | *M.* 3,000, *m.p* 75–76°*C*; *M.* 12,000, *does not flow at* 75°C. *Strong fibres on cold drawing* |
| |  | *Viscous, thermoplastic at low extents of reaction. Higher polymers are insoluble, infusible with no fibre-forming properties* |

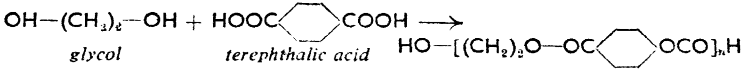
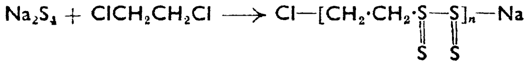
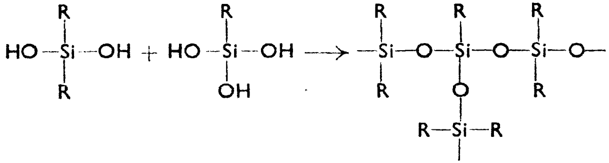
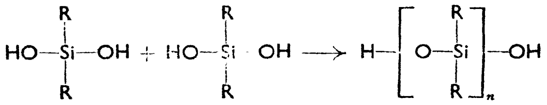
| | | |
|---|---|---|
| |  glycol; terephthalic acid | Strong, pliable fibre on cold drawing high molecular weight material. M.p ~ 250°C |
| Polyanhydride | $HOOC{\cdot}(CH_2)_8COOH \longrightarrow H{-}[OCO(CH_2)_8CO]_n{-}OH$<br>sebacic acid | M. 600, m.p 82°C. High molecular weight products draw to strong pliable fibres. Decomposed by moisture |
| Polyamides | $NH_2(CH_2)_5COOH \longrightarrow H{-}[NH(CH_2)_5CO]_n{-}OH$<br>ε-aminocaproic acid | Strong, pliable, transparent fibres above M. 7,000 |
| | $NH_2(CH_2)_6NH_2 + HOOC(CH_2)_4COOH \longrightarrow H{-}[NH(CH_2)_6NHCO(CH_2)_4CO]_n{-}OH$<br>hexamethylene-diamine; adipic acid | Similar to above, m.p 263°C |
| Polysulphides |  $Na_2S_4 + ClCH_2CH_2Cl \longrightarrow Cl{-}[CH_2{\cdot}CH_2{\cdot}\underset{\|}{\underset{S}{S}}{-}\underset{\|}{\underset{S}{S}}]_n{-}Na$ | Rubber-like |
| | $Na_2S + ClCH_2{\cdot}CH_2Cl \longrightarrow Cl{-}[CH_2{\cdot}CH_2S]_n{-}Na$ | Crystalline |
| Polysilicones |  | Grease-like to hard thermosetting compositions. Stable at high temperatures, non-crystalline, soluble, and thermoplastic |
| |  | |

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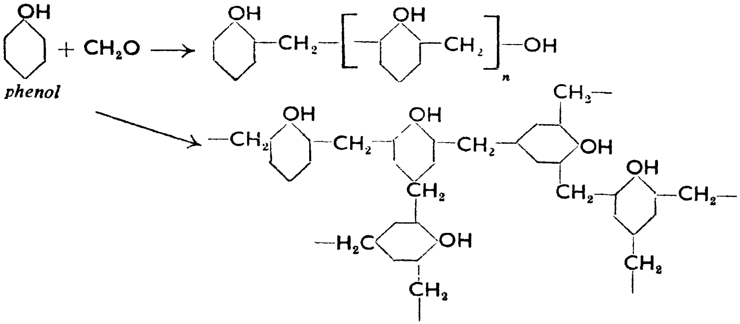
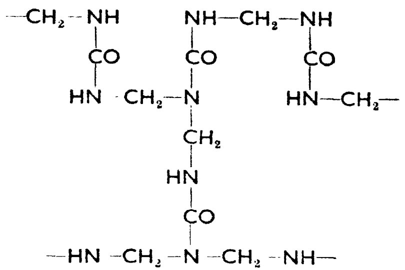
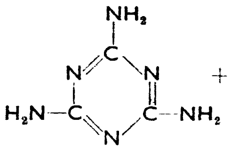
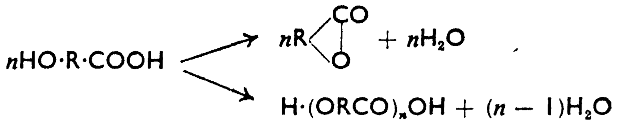
*Table I* (continued)

| *Type* | *Example* | *Properties* |
|---|---|---|
| *Phenol-formaldehyde* |  | *Thermosetting, insoluble, infusible (chemical structure uncertain)* |
| *Urea-formaldehyde* | $H_2NCONH_2 + CH_2O \longrightarrow$<br>urea<br> | *Insoluble, infusible (structure doubtful)* |
| *Melamine-formaldehyde* | <br>$+ CH_2O \longrightarrow$ *Reaction probably similar to above* | *Thermosetting, stable* |

and is related to the nature of the reaction—esterification, amidation, *etc*—by which they are formed. In many cases, however, where the chemical process is not straightforward, as in the reactions of aldehydes with phenol or urea, individual names such as 'phenol-formaldehyde', 'urea-formaldehyde', are employed for these polymers.

It will be observed that many of the monomers listed in *Table I* might give rise to ring compounds, rather than polymers, by internal condensation. In conformity with the general principles of the formation of ring systems, this is observed with 5- and 6-membered compounds, and although larger ring compounds can be formed, they are not common and can usually be readily transformed to linear polymers. Thus, the hydroxyacids form either lactones or linear polymers



$$nHO{\cdot}R{\cdot}COOH \rightarrow nR\left\langle\begin{array}{l}CO\\ O\end{array}\right. + nH_2O \qquad nHO{\cdot}R{\cdot}COOH \rightarrow H{\cdot}(ORCO)_nOH + (n-1)H_2O$$

For example, $\gamma$-hydroxybutyric acid ($HO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$) forms a lactone which does not give rise to a polymer even on hydrolysis. $\gamma$-Hydroxyvaleric acid also forms a lactone, but in the presence of small amounts of water it readily polymerizes to a polyester. In general, if the ring requires less than five or more than seven atoms for its formation, the open-chain polymer is preferred, except when polymerization is conducted at high dilution.

The broad division of the polymers into linear and three-dimensional structures is evident from *Table I.* Planar (two-dimensional) structures are not known among organic systems, although familiar to the inorganic chemist in the case of silicates, mica, asbestos, and graphite. It is not inconceivable that they may be synthesized from aromatic ring systems.

The two general types of condensation polymer exhibit very different properties. Linear condensation products show highly orientated solid structures, as revealed by X-ray examination. They swell readily in suitable solvents, with the formation of homogeneous solutions, and the lower chain lengths are characterized by well defined melting ranges. Since it is not possible in practice to take the polymerization to completion, the theoretical possibility of an 'infinitely' long molecule with a terminal group at each end is not realizable in practice and therefore linear polymers will be of finite molecular weight.

Linear polymers, by their very nature, possess two functional groups per chain, independent of its length. With polymers formed from polyfunctional reactants the number of groups per molecule increases with the degree of polymerization. This can readily be seen from the following schematic representation of the polymerization of a trifunctional monomer to a hexamer (*Figure 2*). The structure may be continued still further by intermolecular reaction between the unreacted groups of the *n*-mer, and it is easy to see that structures of macroscopic dimensions may be readily formed. Giant three-dimensional networks may thus be built up at relatively early stages of the reaction. Their sizes will depend on the amount of the sample being investigated and the extent of reaction, and will be expressible in terms of grams. When we consider that the gram molecule contains $10^{23}$ molecules, these giant molecules can be regarded on the molecular scale as being infinite in size, and are commonly referred to as ' infinite networks '.

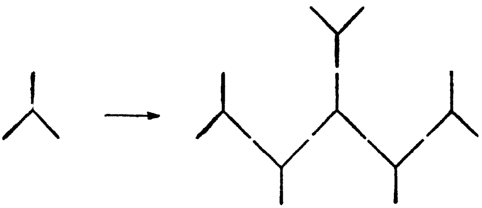


*Figure 2. Schematic representation of one stereoisomeric hexamer from a trifunctional monomer*

There is one further property of polyfunctional reactions which should be mentioned. When, for example, a trifunctional molecule such as glycerol is heated with a dibasic acid, the viscosity of the mixture increases, as the reaction proceeds, at first slowly, and then, at some well defined stage of the process, it rises very sharply, even though most of the reactants still remain unchanged. The product formed at this stage is non-crystalline and infusible, and corresponds to an indefinitely large molecular structure extending throughout the polymerizing mass. The occurrence of this sharp transition from a viscous liquid to a gel at a stage referred to as the ' gel point ' is a characteristic of polyfunctional reactants and has been most satisfactorily explained by the theory of FLORY,[2] who considers it to be due to the incipient formation of an infinite molecular network.

This short introductory survey would not be complete without reference to the great technical importance of both types of condensation polymer. The linear polymers of the polyester or the polyamide type often possess the property of forming strong fibres. They exhibit well defined melting ranges which can be varied by substitution or by change in chain length. Filaments can be readily formed from the viscous melt by an extrusion method or, alternatively, fibres may be spun by the use of fine jets of solutions of the polymer in a volatile solvent. In general, chains of average molecular weight less than 10,000 do not form strong or pliable fibres. With all crystalline chain polymers, the strength of the fibre can be considerably increased by stretching—a phenomenon referred to, by analogy with metals, as cold drawing. This is associated with a re-orientation of the crystalline regions of the thread under the influence of a longitudinal force. This orientation can be directly observed by x-ray studies (Chapter 6), and the extent of cold drawing may be several hundred per cent. The resulting fibres are strong, tough, and elastic, and are of great commercial importance.

The properties of products formed in polycondensation processes depend very much on the molecular weight, and thus on the degree to which the reactants have been polymerized. Heating of low or medium molecular weight polymers leads to further condensation, and with products formed from polyfunctional reactants the material becomes transformed into hard, insoluble products. It is upon this property that the technical use of these materials to give ‘ thermosetting plastics ’ depends. The medium molecular weight materials on warming form a plastic mass, which may be shaped and transformed into a compact, hard, insoluble material on further heating (hardening). The most important members of this class are the phenol-aldehyde, urea-formaldehyde, melamine-formaldehyde, and glycerol-polybasic acid polymers.

### ADDITION POLYMERIZATION

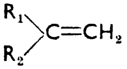
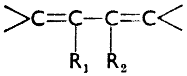
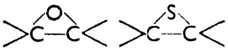
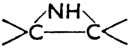
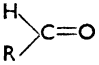
Addition polymers are formed by intermolecular reaction of the monomer units without the elimination of atoms or groups. For example, styrene (I) will readily combine with itself to give a high polymer (II), the process giving no indication as to the nature

$$\underset{\text{I}}{nC_6H_5{\cdot}CH{=}CH_2} \longrightarrow \underset{\text{II}}{-[C_6H_5CH{-}CH_2]_n-}$$

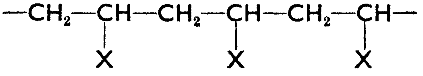
of the groups at the end of the chain. The high polymer is produced by a chain reaction which usually requires initiation, although there is very strong evidence that many pure monomers will undergo spontaneous polymerization without the intervention of a catalyst. As stated previously, addition polymerization is confined entirely to certain classes of unsaturated molecule, namely, the olefins and their derivatives (alcohols, esters, ethers, acids, *etc*, aromatic substituted olefins), the dienes, acetylenes, and certain aldehydes. No material advantage would accrue from a presentation of the very long list of types of monomers which undergo this type of addition polymerization but, in order to understand the general principles of their formation, a summary of the more important unsaturated structures which are very susceptible to this form of reaction is given in *Table II.*

*Table II*

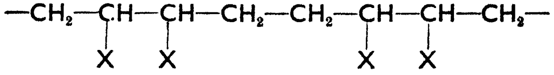
*Addition Polymerization*

| *Structural type* | *Substituent* | *Typical monomer* |
|---|---|---|
|  | $R_1$, $R_2$ = H *or alkyl group* | *Ethylene, isobutene* |
| | $R_1$ = COOH, COOR′. $R_2$ = H, *alkyl or aryl group* | *Acrylic acid derivatives* |
| | $R_1$ = H. $R_2$ = —OCOR | *Vinyl esters* |
| | $R_1$ = *halogen or* CN. $R_2$ = H *or halogen* | *Vinyl halides, cyanides* |
| | $R_1$ = OR′. $R_2$ = H | *Vinyl ethers* |
| | $R_1$ = *phenyl.* $R_2$ = H *or phenyl.* | *Styrene, diphenyl ethylene* |
| | $R_1$ = H. $R_2$ = $—N(R')^2$ | *Substituted vinyl amines* |
|  | *Unsaturated cyclic compounds* | *Indene, coumarone* |
| | *Alkyl, aryl, or halogen groups attached at all positions* | *Butadiene, isoprene, chloroprene* |
| | *Unsaturated ring* | *Cyclopentadiene* |
|  | — | *Ethylene oxide, sulphide* |
|  | — | *Ethylene imine* |
|  | R = H *or alkyl group* | *Formaldehyde, butyraldehyde* |
| $R_1C{\equiv}CR_2$ | $R_1$ = H, $R_2$ = H, *phenyl*<br>$R_1$ = $R_2$ = Cl | *Acetylene and substituted acetylenes* |
| $H_2C{=}CH{-}C{\equiv}CH$ | *See* Table IV | *Vinyl acetylene* |
| $H_2C{=}CH{-}C{\equiv}C{-}CH{=}CH_2$ | — | *Divinyl acetylene* |

*Molecular Structure of Addition Polymers*—The monomeric units which unite to form the macromolecule are linked by covalent bonds. Confining our attention to truly linear structures, it is possible that the simple units can link up in a regular or a random manner. Selecting a monomer, $CH_2{=}CHX$ for illustration, it is seen that two regular arrangements are possible—namely, head-to-tail (I), head-to-head or tail-to-tail (II):

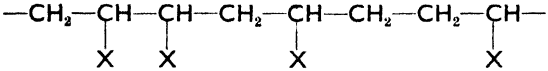


$$-CH_2-\underset{X}{CH}-CH_2-\underset{X}{CH}-CH_2-\underset{X}{CH}- \quad . \ . \ . \ . \qquad (I)$$



$$-CH_2-\underset{X}{CH}-\underset{X}{CH}-CH_2-CH_2-\underset{X}{CH}-\underset{X}{CH}-CH_2- \quad . \qquad (II)$$

and a series of random structures of the following type (III)



$$-CH_2-\underset{X}{\underset{|}{C}H}-\underset{X}{\underset{|}{C}H}-CH_2-\underset{X}{\underset{|}{C}H}-CH_2-CH_2-\underset{X}{\underset{|}{C}H}- \quad . \quad \text{(III)}$$

The actual structure which may be formed in any particular case cannot be predicted from the nature of the monomer, nor do stereochemical considerations play a decisive role. In fact, the elucidation of the configuration has generally to be established by the orthodox methods of organic chemistry supplemented by reactivity measurements and molecular structure determinations by physical methods. The conclusions reached from a large number of investigations [3] show that methyl vinyl ketone, methyl isopropyl ketone, vinyl acetate and alcohol, vinyl chloride, vinyl bromide, and styrene polymers have the head-to-tail structure (I). In the case of the alkyl α-halogen-acrylates there is evidence for structure II or III, but the question is still unsettled.

It must always be borne in mind that the chemical structural determinations carried out on molecules made up of hundreds of simple units cannot establish that no irregularities of the general structure, or possibly slight side branches of the chains, are present. They indicate only the predominant structure of the chain. Recent evidence indicates that a small percentage of the groups in polymers such as vinyl acetate are arranged in other than the simple head-to-tail form.[4]

These observations also leave the nature of the end groups an open question. Much work has been done recently in this respect. In many cases of catalyzed initiation it has been shown that fragments of the catalyst molecule are attached to the end of the chain (Chapter 3). These observations provide important evidence as to the nature of the initiation process and, in principle, determination of the number of end groups should permit an exact deduction as to the degree of polymerization, as is possible with the shorter polyester chains where each chain carries one carboxyl group. The difficulty of similar measurements with the longer vinyl polymer chains is very great and only in a few cases has this been achieved (Chapter 5).

## STRUCTURE AND POLYMERIZABILITY

The tendency of a molecule to polymerize depends greatly on the nature and position of the substituents on the double bond. For instance, the substitution of one or both hydrogens in ethylene by chlorine, to give vinyl or vinylidene chloride, very markedly increases the ease of polymerization of the molecule. The measure of these relative tendencies is the rate of polymerization under comparable conditions. This overall rate is, however, a composite rate of the elementary reaction processes comprising initiation, propagation, and termination of the chain, and hence for any true comparison of reactivity, the rates of the individual steps are, in principle, necessary. It would then be possible to specify which of the stages was modified by change of structure. At present this information is lacking, although a step forward has recently been made by MELVILLE and JONES,[5] who have measured the relative rates of propagation of a number of vinyl compounds in the vapour phase, reaction being initiated by photochemically formed free radicals. Their results are summarized in *Table III*.

*Table III*

| *Compound* | *Vinyl chloride* | *Butadiene* | *Styrene* | *Acrylic nitrile* | *Methyl iso-propenyl ketone* |
|---|---|---|---|---|---|
| *Relative tendency to polymerize by free radical mechanism* . | 1 | 5·5 | 9 | 10 | 33 |

Until more extensive and systematic kinetic results are available, the comparison between structure and tendency to polymerize can be formulated only on a qualitative basis. A careful survey of the available data has shown that there are certain guiding principles or empirical rules which have been of much value in the synthesis of high polymers. These are important from the kinetic aspect, and will be summarized briefly in the following paragraphs.

*Ethylenic Derivatives*—The introduction of negative groups into ethylene molecules usually increases the ease of polymerization; for example, F, Cl, Br, I, CN, CHO, COOH, $C_6H_5$. Alkyl groups do not have any pronounced effect, and the higher olefins, except in the presence of powerful ionic catalysts, polymerize with difficulty. When more than one substituent is introduced, the reactivity varies with the relative positions of the two groups. Symmetrically substituted derivatives, in general, do not polymerize, whereas the corresponding unsymmetrical substituted products do so with ease. Thus, for instance, vinylidene chloride, $CH_2{=}CCl_2$, is not very different in reactivity from vinyl chloride, $CH_2{=}CHCl$, but the trichloro derivative $CHCl{=}CCl_2$ does not polymerize. In fact, with the exception of tetrafluoroethylene (and possibly other compounds in which hydrogen is replaced by fluorine), it may be stated that the presence of an unsubstituted $CH_2$ in the olefinic molecules is a necessary condition for polymerization.

Recently, the effect of substitution in the chain and ring of styrene on the tendency to polymerization has been investigated by MARVEL and his co-workers.[6] The general conclusions which can be drawn from these results are:

*1* substitution in the side chain at either the α or β position decreases the reactivity or inhibits polymerization entirely (*e.g.* α-chlorostyrene and β-bromostyrene);

*2* substitution in the ring by Cl, CN, or COOH increases the tendency to polymerization, whereas the introduction of a nitro group into the ring inhibits reaction.

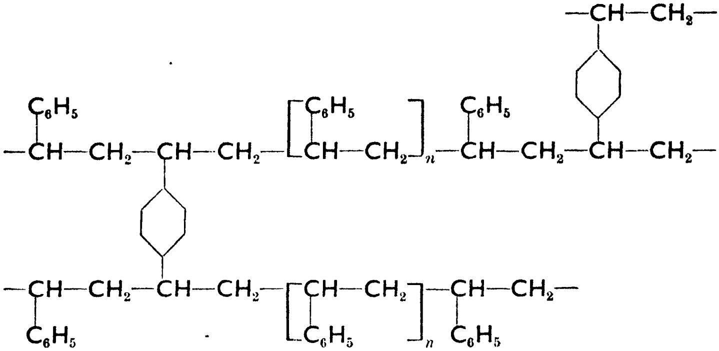
It is not clear to what extent these polymerizations, which occur by a free radical mechanism, are affected by orientating influences in the aromatic ring. A detailed quantitative kinetic investigation of these reactions would provide most valuable information.

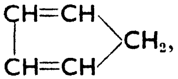
*Diolefins*—The polymerizability of diolefins is determined by the relative positions of the double bonds. The high reactivity of the conjugated diolefins, such as butadiene, is familiar; conjugation between the side chain and an unsaturated ring, *e.g.* as in vinyl cyclohexene, leads to 1 : 4-polymerization, as in butadiene. 1 : 2-Diolefins, such as allene or methyl allene, on the other hand, polymerize with great difficulty. Substitution in the diolefin has a marked influence on reactivity. This has been shown by CAROTHERS and his collaborators [7] in their extensive investigations on the effect of substitution of the hydrogen atoms in butadiene by halogen and alkyl groups. The relationships are very complex, and no simple principle which enables the effect of substitution on the polymerizing molecule to be foretold, can be formulated.

Whereas conjugated dienes usually polymerize predominantly as if only one of the double bonds were participating in the reaction, *viz*

$$H_2C{=}CH{-}CH{=}CH_2 \longrightarrow -[CH_2{\cdot}CH{=}CH{\cdot}CH_2]_n-,$$

divinyl derivatives of the type of divinyl benzene give highly cross-linked structures. In fact, cross links may be readily introduced into a vinyl polymer by the addition of small amounts of a divinyl compound. Thus, styrene to which has been added 0·01 per cent *p*-divinyl benzene gives an insoluble polymer, and the following formula illustrates the formation of a kind of divinyl bridge linking the chain molecules of the polystyrene:

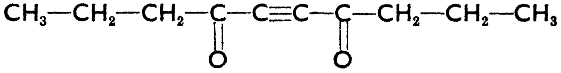


*Cyclic Compounds*—Highly unsaturated cyclic compounds show a great tendency to polymerize. These compounds can be regarded as symmetrically disubstituted ethylene derivatives, and polymerize more readily than the corresponding straight chains, especially if the ring is 5-membered—*e.g.* cyclopentadiene,  $\begin{matrix} CH{=}CH \\ | \\ CH{=}CH \end{matrix}\!\!>CH_2$, shows greater reactivity than piperylene, $H_2C{=}CH{-}CH{=}CH{-}CH_3$. The tendency for indene and coumarone to polymerize may, in a similar manner, be associated with the presence of the unsaturated 5-membered ring. Other ring and partly condensed structures, such as substituted naphthalenes and anthracenes, which display an unsaturated character, also show a marked tendency to polymerize.

*Acetylene Compounds*—In comparison with the vinyl compounds, our knowledge of the polymerizability of compounds containing the triple bond is very sparse. In view of the recent developments in the investigation and technical production of acetylenic derivatives, a new interest has developed in this field, and it is therefore useful at this stage to review the polymerization reactions of this class of compounds.

In the absence of activating influences, the triple bond is comparatively less reactive than the double bond. Direct thermal polymerization of acetylene (400–1150°C) in the absence, and also in the presence of solid catalysts, gives rise to a complicated series of products, many being of the ring-structure type. Copper and magnesium containing catalysts bring about polymerization at relatively low temperatures, giving an insoluble inert powder—cuprene—of unknown composition. Very recently it has been shown that acetylene, in an inert solvent such as tetrahydrofuran and in the presence of nickel compounds, undergoes cyclic polymerization to cyclooctatetraene, which may itself be polymerized to resinous products.

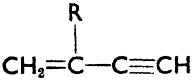
Very little information is available on the effect of substitution in the acetylene molecule on polymerizability. The introduction of an aromatic grouping increases the activity of triple bonds, but it still does not approach that of the double bond in its polymerization tendency. Thus, phenyl acetylene, $C_6H_5{\cdot}C{\equiv}CH$, is much more difficult to polymerize than styrene, $C_6H_5CH{=}CH_2$. Conjugated acetylene groups—*e.g.* diacetylene, $HC{\equiv}C{-}C{\equiv}CH$—are extremely reactive and polymerize rapidly without activation at 0°C. Recently it has been shown that the keto and hydroxyl groups exercise a considerable activating influence on the triple bond. For instance, the compound,



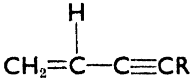
$$CH_3{-}CH_2{-}CH_2{-}\underset{O}{\underset{\|}{C}}{-}C{\equiv}C{-}\underset{O}{\underset{\|}{C}}{-}CH_2{-}CH_2{-}CH_3$$

undergoes extensive polymerization on distillation. Similarly, dichloroacetylene polymerizes much more readily than acetylene, the low molecular weight molecule hexachlorobenzene being one of the main products.

*Vinyl Acetylene*—Much of the literature on the polymerization of triple bond compounds refers to the conjugated vinyl acetylene system. Vinyl acetylene and its substituted derivatives,



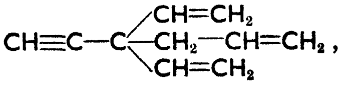
$CH_2{=}\overset{R}{\overset{|}{C}}{-}C{\equiv}CH$ and



$CH_2{=}\overset{H}{\overset{|}{C}}{-}C{\equiv}CR$ (R = alkyl or halogen group), polymerize thermally at 100–120°C, and on standing at room temperatures; the isolated products in these cases are low molecular weight compounds containing cyclobutane rings. Under similar conditions, divinyl acetylene polymerizes readily, giving dimers and low molecular weight products. Both vinyl propiolic acid and vinyl isopropiolic acid polymerize to a rubber-like substance of unknown structure.

The tendency to polymerization is not restricted to the conjugated double-triple bond systems. The hydrocarbons,

$Ph{-}C{\equiv}C{-}CH_2{-}CH{=}CH_2$ and

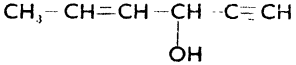
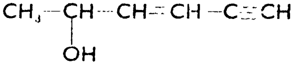
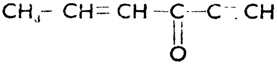
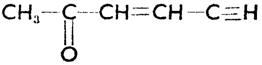
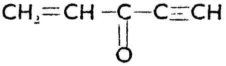
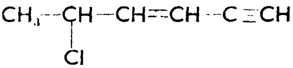


$CH{\equiv}C{-}C\!\left<\begin{matrix}CH{=}CH_2\\CH_2{-}CH{=}CH_2\\CH{=}CH_2\end{matrix}\right.$,

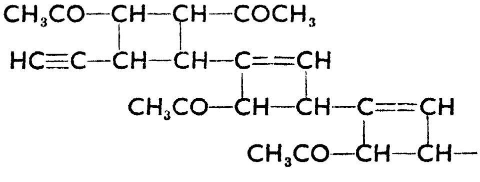
have been reported to resinify on standing.

Recently, the author and Dr G. H. Kington have investigated the polymerization of a number of acetylenic compounds. The following table summarizes some of their results.

*Table IV*

| *Substance* | *Formula* | *Polymerization products* |
|---|---|---|
| *Propenyl ethinyl carbinol* |  $CH_3{-}CH{=}CH{-}\underset{OH}{\underset{\vert}{CH}}{-}C{\equiv}CH$ | *With* 1% *benzoyl peroxide*<br>*No polymerization at* 90°<br>*Slight polymerization at* 150°C |
| *Hex-3en-5yn-2ol* |  $CH_3{-}\underset{OH}{\underset{\vert}{CH}}{-}CH{=}CH{-}C{\equiv}CH$ | *Rapid polymerization at* 150°C |
| *Propenyl ethinyl ketone* |  $CH_3{-}CH{=}CH{-}\underset{O}{\underset{\Vert}{C}}{-}C{\equiv}CH$ | *Viscous oil in* 23 *hours* |
| *Hex-3en-5yn-2one* |  $CH_3{-}\underset{O}{\underset{\Vert}{C}}{-}CH{=}CH{-}C{\equiv}H$ | *Rapid with* 1% *tert.-butylhydroperoxide at* 65°C<br>*Solid resin on standing* (24 *hours*) |
| *Vinyl ethinyl ketone* |  $CH_2{=}CH{-}\underset{O}{\underset{\Vert}{C}}{-}C{\equiv}CH$ | *Solid resin in* 2 *hours with* 1% *tertiary butylhydroperoxide* |
| 2-*Chloro-hex-3en-5yne* |  $CH_3{-}\underset{Cl}{\underset{\vert}{CH}}{-}CH{=}CH{-}C{\equiv}CH$ | *Black viscous oil in* 9½ *hours at* 20°C |

The structure of the above polymers has not yet been completely elucidated, but with products of molecular weights 1,000–1,500 both double and triple bonds remain in the polymer. The most probable structure of the polymer is one containing butene rings, *e.g.*



*etc,*

although there is evidence of the presence of other types of structural unit.

## COPOLYMERS

It is well known that polymerization of mixtures of monomers produces polymers in which both types of reacting units are incorporated in the chain—*e.g.* vinyl chloride and vinyl acetate. The resulting polymers have physical and mechanical properties markedly different from those of a mixture of the polymers which would be formed from the separate monomers. Not every pair of polymerizable monomers will copolymerize. Some unsaturated monomeric derivatives, which do not themselves polymerize, enter into copolymers—*e.g.* maleic acid esters will not polymerize to give chains, but will readily copolymerize with styrene. Since the two monomers do not enter the chain at the same rate, the polymer formed will not have the same composition as the monomer mixture from which it was formed. There is probably a difference in composition along each polymer chain formed, due to rapidly changing composition of the unpolymerized monomer mixture as the reaction proceeds. Furthermore, owing to the same causes, the average composition of the polymer chains will vary with the stage to which the polymerization is conducted. For these reasons exact structural determinations with copolymers are difficult, but results on the whole support the above conclusions.

## COMPARISON OF CONDENSATION AND ADDITION POLYMERIZATIONS

The general classification of high polymers as being of the condensation or addition type was based on the relationships between the composition of the monomer and the polymer. The distinction between these types is more strikingly emphasized by the kinetic characteristics of the polymerization processes, and it is of interest to compare these differences.

Condensation polymers may be formed by a wide variety of reactions, the nature of which establishes the structure of the polymer, whereas addition polymers are formed by a single type of reaction. The synthesis of a condensation polymer is accomplished by a series of similar stepwise reactions, and the average molecular weight of the product increases as the reaction proceeds. Thus, in the simple case of the polyesterification of a hydroxy acid, the first step is the formation of a dimer by intermolecular esterification,

$$\mathrm{HO{\cdot}R{\cdot}COOH + HO{\cdot}R{\cdot}COOH \longrightarrow HO{\cdot}R{\cdot}COOR{\cdot}COOH + H_2O}$$

This step is followed by a second similar process in which a further molecule of monomer reacts to give a trimer, or the dimer may react with another dimer to give a tetramer, and so on. The total reaction is made up of a general series of inter-reactions between all species present, from monomer upwards. Each of these unit reactions is of the same type, and can be regarded as a reaction between the OH and COOH groups, independently of the remainder of the molecule. Kinetically, therefore, each reaction step can be assumed to possess equal rate constants.

Addition reactions of vinyl-type monomers proceed by a chain mechanism. Once the monomer (M) has been activated (M*), addition reactions proceed successively, according to

$$\mathrm{M} \longrightarrow \mathrm{M}_1{}^* \longrightarrow \mathrm{M}_2{}^* \longrightarrow \mathrm{M}_3{}^* \longrightarrow \mathrm{M}_n,$$

until the chain is terminated. The long chain is formed in a single rapid reaction sequence, and thus the full size polymer molecule is produced from the earliest stages of the reaction. The polymer so formed does not usually increase in size with time of reaction; time merely determines the extent of conversion of the monomer to polymer. This process is in sharp contrast to condensation polymerization, in which the size of the polymeric molecule increases with the extent of reaction, and the process may be interrupted at any time to give a polymer of the molecular weight desired. Furthermore, in order to obtain high molecular weight products in condensation polymerizations, it is necessary to continue the reaction until polymerization is almost complete; even then the molecular weights of the products are small, relative to those obtained in some vinyl polymerizations.

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## CHAPTER 2

# CONDENSATION POLYMERIZATION

LARGELY DUE TO the pioneering investigation of W. H. CAROTHERS and his collaborators [1] and the recent experimental and theoretical investigations of RAFF, DOSTAL, MARK, KIENLE, FLORY, and STOCKMAYER,[2] the basic principles of condensation polymerization have been soundly established. These studies have revealed the relative simplicity of the reaction mechanism and the possibility of synthesizing macromolecules of known structure. The elementary condensation reactions, such as esterification, have been thoroughly studied in the past, and the polymerization process, which proceeds by a succession of stepwise condensation reactions, introduces no new feature. Bifunctional reactants can be polymerized to give strictly linear molecules, and by a suitable choice of starting materials the polymer structure can be varied at will. In contrast to addition polymerizations, the average molecular weight may be controlled by varying the degree of polymerization. Furthermore, by use of the basic postulate of equal reactivity of similar functional groups, independent of the size of the molecule to which they are attached, the molecular size distributions can be evaluated accurately. These are the features which enable the simple condensation polymers, in spite of their molecular heterogeneity, to be characterized completely. They provide an ideal starting point for the investigation of the relationship between polymer structure and physicochemical properties. The general types of condensation polymer have already been summarized in Chapter 1 (see *Table I*), and it is the purpose in this section to review the development of the general basis of the mechanism of formation and the properties of these polymers. The relationships between molecular structure and the properties of the solid state will be dealt with in Chapters 6 and 7.

### KINETICS OF CONDENSATION POLYMERIZATIONS

The close similarity between polyfunctional condensations and the extensively studied monofunctional reaction has already been pointed out in Chapter 1. Investigations have shown that both types of reaction occur under similar conditions of temperature and catalysis, and at comparable rates. In fact, the results have established the important conclusion that the primary reaction between the various species of molecule is that of reaction between the functional groups, and is independent, except in the initial stages of the reaction, of the nature and length of the chain to which the functional group is attached. We shall first consider the experimental evidence provided by esterification studies.

*Polyesterification*—Polyesterification reactions are usually studied under conditions in which the water formed is continuously removed. The rate of reaction can be followed by titration of the unreacted carboxyl groups in samples removed from the mixture at various times. Thus, in the self-esterification of an hydroxy acid to a linear polymer, every molecule, independent of its size, will contain one carboxyl group. It is usual to express the result in terms of the extent of reaction $p$, which is defined as the fraction of functional groups which have been esterified at the time of removal of the sample. Thus, if $N_0$ is the initial number of reactive groups and $N$ the number of unreacted groups remaining at time $t$, then

$$p = \frac{N_0 - N}{N_0}$$

We shall select, as a typical example, the reaction between equivalent amounts of a dibasic acid and a glycol. As with simple esterifications, the reaction is catalysed by acid. In the absence of added hydrion catalyst, the rate of reaction will be proportional to the product of the hydroxyl and the square of the carboxyl concentrations, since under these conditions a molecule of the acid undergoing esterification functions as a catalyst. Therefore, if $C$ is the concentration of reacting groups,

$$\text{Rate of Esterification} = -\frac{dC}{dt} = k[\mathrm{OH}][\mathrm{COOH}]^2$$
$$= kC^3$$

where $k$ is the specific reaction velocity constant. Integrating and introducing the condition that when $t = 0$, $C = C_0$, the expression for the rate is

$$2kt = \frac{1}{C^2} - \frac{1}{C_0{}^2}$$

If it is assumed that the effect of the water formed during esterification is negligible—that is, no effect on concentration occurs due to the volume decrease resulting from the loss of water—then $C$ may be replaced by $C_0(1 - p)$ and the rate expression becomes

$$2ktC_0{}^2 = \frac{1}{(1 - p)^2} - 1$$

Thus, the plot of $\frac{1}{(1 - p)^2}$ should increase linearly with $t$ if $k$ does not vary with change of size of the reacting species. This relationship has been established by FLORY[3] for the esterification of a number of glycols with adipic acid and for the polymerization of ω-hydroxy-undecanoic acid. *Figure 3* shows the results for the reaction of diethylene glycol with adipic acid. The esterification of the monobasic acid, caproic acid, is represented on the same diagram, and comparison shows clearly the close similarity between this reaction and the reaction giving rise to polymers. The monofunctional reaction is slower owing to the greater equivalent weight of reactive groups, resulting in dilution of the monofunctional reactant with inert hydrocarbon chains. The curves for the caproic and adipic acid are superimposable by multiplying all time units for one of them by a constant factor. This similarity is also borne out by other analogous bi-bi-, mono-bi-, and mono-mono-functional reactions studied by FLORY[4] and by BAKER, FULLER, and HEISS.[5]

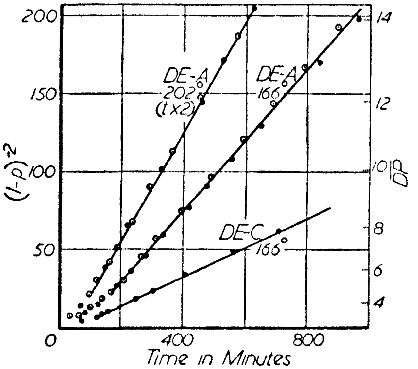


*Figure 3. Diethylene glycol/adipic acid (DE-A) and diethylene glycol/caproic acid (DE-C) reactions. The time scale at 202°C has been multiplied by two*

(*Reference* : 3)

In the case of acid-catalysed reactions the rate of reaction is proportional to the hydroxyl, carboxyl, and catalyst concentrations,

and therefore
$$-\frac{dC}{dt} = k'C_{cat}C^2$$

Since the catalyst concentration is constant, integration gives

$$\frac{1}{C} = k''t + \frac{1}{C_0}, \quad \text{where} \quad k'' = k'\,C_{cat}$$

and since
$$C = C_0(1-p),$$

$$k''tC_0 = \frac{1}{1-p} - 1$$

The linearity of the plot of $\frac{1}{1-p}$ against $t$ (*Figure 4*) has been established by Flory[3] for a number of polyesterifications and for molecular weights of polymer up to 10,000. The results of some typical esterifications and polyesterifications[3] are summarized in *Table V.*

*Table V*

| *Reaction* | $k_{202°C} \times 10^{-2}$ *(equiv./ 1,000 g)*$^{-1}$ *min*$^{-1}$ |
|---|---|
| HO—$(CH_2)_2$—O—$(CH_2)_2$OH + HOOC$(CH_2)_4$COOH | 0·41 |
| ,, + H$(CH_2)_4$COOH | 0·35 |
| HO—$(CH_2)_2$—OH + HOOC$(CH_2)_4$COOH | 0·5 |
| HO—$(CH_2)_{10}$—OH + ,, | 1·63 |
| HO—$(CH_2)_{12}$—OH + ,, | 1·57 |
| H—$(CH_2)_{12}$—OH + H$(CH_2)_{11}$COOH | 2·5 |

The general conclusion from these results is that the polycondensation proceeds in parallel manner to the monofunctional reactions, and that the reactivity of the functional group is essentially independent of the size of the molecule. This is in general accord with the theory of organic reactions, which postulates that in any hydrocarbon chain, the effect of substitution in the molecule does not extend very far along the chain. Thus, we should expect that in the esterification of a series of fatty acids with the same alcohol, the reaction rates would change with the first few members and then remain sensibly constant. This is strikingly borne out by the results of FAIRCLOUGH and HINSHELWOOD[6] for the hydrion and undissociated acid-catalysed esterification of a number of fatty acids in ethyl and methyl alcohols, shown in *Table VI* (p. 27).

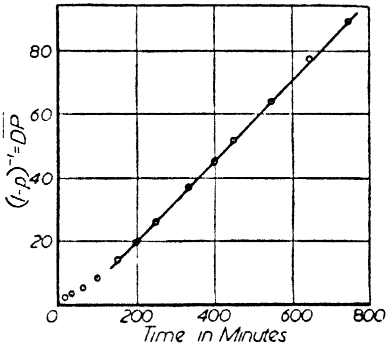


*Figure 4. Reaction of diethylene glycol with adipic acid at* 109°*C catalysed by* 0·4 *mol per cent of* p-*toluene sulphonic acid*

(*Reference* : 3)

In comparison with bifunctional condensations, few kinetic measurements have been made on the technically important group of polycondensation reactions which lead to three-dimensional structures. KIENLE and his co-workers[7] have measured the rate of reaction of glycerol with a series of dibasic acids by determination of both the carboxyl-group concentration, and the water formed, as a function of the extent of reaction. They show that the reaction occurs, as with bifunctional monomers, primarily by inter-esterification, although the course is modified by intra-esterification and anhydride formation. They conclude that the reaction occurs in a stepwise manner and that when gelation sets in the average molecular weight corresponds to that of tetramers.

Recently T. T. JONES[8] has studied the kinetics of the initial phases of the reaction of phenol and formaldehyde in aqueous media. The reaction takes place in a stepwise manner, and two types of reaction may be distinguished, *1* a reaction of formaldehyde and phenol to form phenolic alcohols and *2* a subsequent condensation of these phenolic compounds with phenol to form larger molecules.

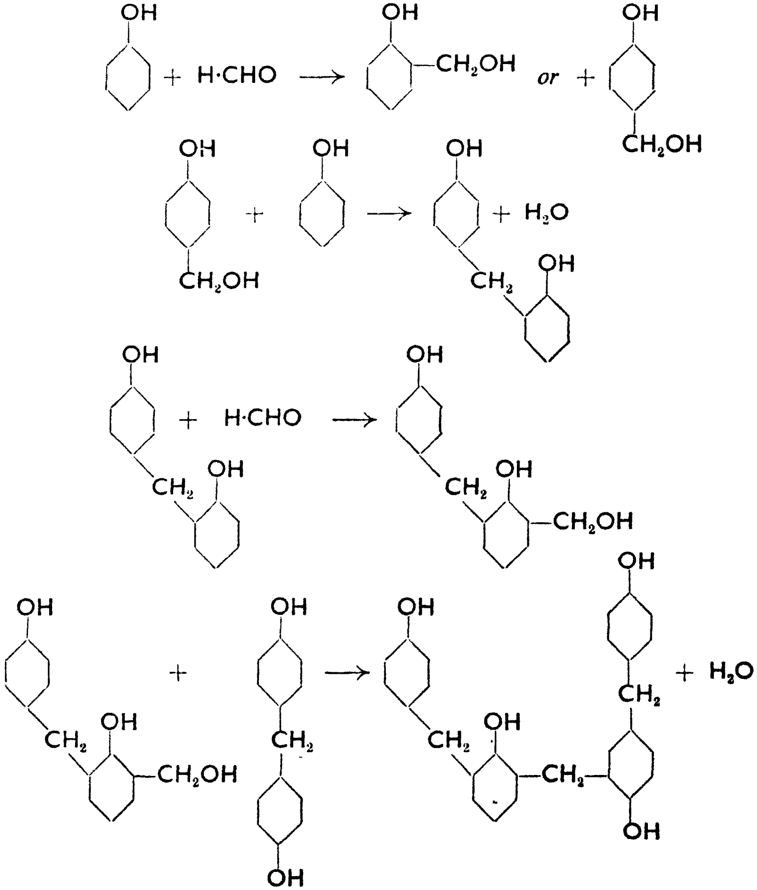


*Table VI*

| *Acid* | *Catalysis by undissociated acid in ethyl alcohol* | | *Catalysis by hydrion in methyl alcohol* | |
|---|---|---|---|---|
| | *E (cal)* | $k_{100°C} \times 10^4$ *(litre mol⁻¹ sec⁻¹)* | *E (cal)* | $k_{20°C} \times 10^3$ *(litre mol⁻¹ sec⁻¹)* |
| *Acetic* | 15,200 | 5·70 | 12,450 | 4·42 |
| *Propionic* | 15,000 | 4·47 | 11,000 | 3·84 |
| *Butyric* | 14,800 | 3·00 | 11,800 | 2·28 |
| *Hexoic* | 15,100 | 3·39 | 11,700 | 2·08 |
| *Pelargonic* | 14,900 | 3·80 | 11,300 | 1·98 |
| *Myristic* | 14,800 | 3·99 | — | — |
| *Palmitic* | 15,100 | 4·27 | 11,800 | 2·21 |
| *Behenic* | 15,100 | 4·27 | — | — |

The reaction occurs under the influence of both acid and basic catalysts. With HCl as catalyst and at 80–100°C the rate law over a range of *p*H's is second order. At 30°C the rate law approaches first order, owing to a change in the course of the reaction which now gives rise to the formation of dialcohols. In the initial stage the reaction follows a similar course to the bifunctional esterification, but as the extent of reaction increases the occurrence of additional reactions makes the kinetic treatment difficult. A large amount of work remains to be done before the complete reaction mechanism can be understood.

*General Kinetics of Polyreactions*—The detailed treatment of polyesterification reactions given in the foregoing section may now be generalized.[9] The type of reaction may be represented symbolically by

$$\mathsf{M}_x + \mathsf{M}_y = \mathsf{M}_{x+y}$$

where both $x$ and $y$ can assume all values from unity to large numbers. Assuming that all functional groups have approximately the same reactivity, each reaction step can be assigned the same velocity constant, $k$. This is the only assumption necessary to derive the general kinetic equation and, as we have already seen, it is in agreement with the experimental facts.

Starting from the monomer $\mathsf{M}_1$, reaction can occur with itself and with molecules of all other chain lengths. The rate of disappearance of monomer will therefore be given by the following equation wherein $M_1$ denotes the monomer concentration

$$-\frac{dM_1}{dt} = kM_1(M_1 + M_2 + M_3 + \ldots)$$

$$= kM_1 \sum_{n=1}^{\infty} M_n \quad \ldots\ldots\ldots \quad (1)$$

Dimers are formed only by reaction between monomers, but may be consumed by reacting with molecules of all other lengths. Hence

$$\frac{dM_2}{dt} = \tfrac{1}{2}kM_1{}^2 - kM_2 \sum_{n=1}^{\infty} M_n$$

(The factor $\frac{1}{2}$ is necessary because two monomers must be used to produce a dimer.)

Similarly, for the reaction of trimers one may write

$$\frac{dM_3}{dt} = \tfrac{1}{2}kM_1M_2 - kM_3 \sum_{n=1}^{\infty} M_n$$

Generalizing this procedure, one obtains for the formation and disappearance of $n$ mers

$$\frac{dM_n}{dt} = \frac{k}{2} \sum_{s=1}^{s=n-1} M_sM_{n-s} - kM_n \sum_{n=1}^{\infty} M_n \quad . \quad . \quad (2)$$

The first term states that $n$ mers are formed by the combination of two smaller molecules, the indices of which add up to $n$. On carrying out the summation one counts each molecule with $s$ smaller than $n - 1$ twice, and hence one has to divide the term by two.

The solution and integration of the pair of equations (1) and (2) result in the following equation for the number of $n$ mers ($N_n$) at any extent of reaction $p$

$$N_n = N_0p^{n-1}(1 - p)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $N_0$ = number of molecules of reactant. The equations give the additional relationship

$$\frac{dp}{dt} = \tfrac{1}{2}N_0k(1 - p)^2$$

or

$$p = \frac{N_0kt}{2 + N_0kt} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

It is often interesting to know the total amounts of polymer produced at various times. This may be deduced from equations (3) and (4). Since the total weight of $n$ mers, $W_n = N_n \,.\, n \,.\, m_0$, where $m_0$ is the molecular weight of the structural unit, the weight fraction of an $n$ mer, $w_n = np^{n-1}(1 - p)^2$. The weight fraction of condensate from dimers upwards is

$$\sum_{n=2}^{\infty} w_n = \sum_{n=1}^{\infty} w_n - w_1$$
$$= 1 - (1 - p)^2 = 2p - p^2$$

or total amount of polymer $= W(2p - p^2)$, where $W =$ total weight of system in grams. This may be expressed in terms of $t$ by substituting for $p$ from (4).

Equation (3) is an expression for the distribution curve of the polymer, and gives the concentration of $N_n$ as a function of $n$ and $p$. This formula may also be derived in a more direct manner by a statistical method (page 32) which brings out much more clearly the physical meaning of the expression. It will be seen that both methods have their particular advantages; the statistical method is preferable if the reaction mechanism is simple, but with the more complicated reactions, such as the vinyl polymerizations, the kinetic method has proved most useful.

## THEORY OF THE REACTIVITY OF LARGE MOLECULES

The velocity of reaction in solution can be expressed in terms of the Arrhenius equation, $k = PZe^{-E/RT}$, where $Z$ is the actual collision rate between molecules and $P$ the probability that collisions between active molecules lead to reaction. Theoretical arguments and experiments indicate that the order of $Z$ is that calculated by the kinetic theory and is the same in the gas phase as in solution.[10] Although the solvent impedes diffusion, and thus cuts down the number of collisions which a given solute molecule makes with others in unit time, it also tends to hem in pairs of solute molecules, and causes them to make repeated collisions with one another, the two effects nearly balancing. The occurrence of collisions in sets has been discussed and illustrated on mechanical models by RABINOWITCH and WOOD,[11] who have shown that the lower the diffusion rate the greater will be both the number of encounters and the time before the molecule diffuses to a new position in which it meets another reactive partner. They conclude that the effects of mobility and collision rate nearly balance, and that the overall collision number remains approximately constant.

FLORY[12] has extended these ideas to polymer molecules. On account of the lower mobility of the large molecules, the number of encounters between functional groups (which will now be determined mainly by the additional factor of the diffusion of the terminal group by rearrangement of the back-bone carbon chain) will be increased before they diffuse to new positions. Other similar series of encounters will follow and about 1 in $10^8$ such collisions between functional groups leads to reaction. Decreased molecular mobility due to size will therefore alter the time distribution of collisions experienced by any functional group, but will not greatly change the average collision rate between functional groups. Since it is the latter which determines the rate of reaction, it follows that, for functional reactions which require perceptible activation, viscosity has no appreciable influence on the collision number except at very high viscosities, when the diffusion of particles becomes the rate determining step.

These conclusions are completely borne out by esterification measurements on a number of fatty acids up to $C_{22}$ (*Table VI*) and by investigations on polycondensations[3] in which it was shown that the velocity constant was unaffected in the formation of polymers of molecular weights up to 10,000, or by an increase in viscosity of the reacting mixture of over 2,000-fold.

## MOLECULAR WEIGHT OF LINEAR CONDENSATION POLYMERS

Since the peculiarities of high polymers are due to the fact that their molecules are very large, estimates of molecular weights are of the utmost importance. The general methods for such determinations are described in detail in Chapter 5.

The molecular weights of condensation polymers have usually been determined by end-group methods.[13] Cryoscopic and ebullioscopic methods[14] have been employed for accurate measurements of molecular weights below 10,000 and the results are in good agreement with end-group methods. Viscosity methods in solution[15] and melt[3] have also been used frequently, although the molecular weight/viscosity relationship, on which the method relies, is usually established by end-group determinations.

In the condensation of bifunctional units, which may generally be written

$$n\mathrm{A{-}B} \longrightarrow \mathrm{A{-}BA{-}BA{-}B{-}}$$

where A and B are functional groups and AB is the linkage formed by condensation, the total number of molecules present will equal the number of unreacted groups A or B, since every molecule, from the monomer to a linear chain of any length, carries one unreacted A or B group at each end of the molecule. The number average molecular weight will be given by the reciprocal of the number of mols of unreacted A or B per gram. The same is true for condensations of the type

$$\mathrm{A{-}A} + \mathrm{B{-}B} \longrightarrow \mathrm{A{-}AB{-}BA{-}A{-}}$$

For either kind of reaction the degree of polymerization, $\overline{DP}$, will be given by the original number of monomer units $N_0$ divided by the total number of molecules present. The latter is equal to the number of unreacted A or B groups, and is given by $N_0(1 - p)$, where $p$ = extent of reaction. For linear polymers formed from equimolar quantities of starting materials

$$\overline{DP} = \frac{1}{(1 - p)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The values of $\overline{DP}$ for various extents of reaction $p$ are shown in the following table.

*Table VII*

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| *% Reaction* . | 0 | 50 | 80 | 90 | 95 | 99 | 99·9 |
| $p$ . . . | 0 | 0·5 | 0·8 | 0·9 | 0·95 | 0·99 | 0·999 |
| $\overline{DP}$ . . . | 1 | 2 | 5 | 10 | 20 | 100 | 1,000 |

It follows that high molecular weights can only be attained by taking the condensation as nearly as possible to completion. Any small amounts of side reaction would, of course, very materially alter the $\overline{DP}$ in the latter region.

For second-order polyreactions it has already been shown (page 24) that

$$C_0 C_{cat} \, . \, k't = \frac{1}{1 - p} - 1$$

Therefore, from equation (5) it follows that

$$\overline{DP} = const \times t + 1$$

The average molecular weight increases linearly with time, as illustrated in *Figure 4*. In a similar manner, for third-order reaction,

$$\overline{DP} = (const \times t + 1)^{\frac{1}{2}}$$

and, except at low degrees of polymerization,

$$\overline{DP} = (const \times t)^{\frac{1}{2}}$$

The average molecular weight now increases only as the square root of the time, and therefore high molecular weights will only be obtained by continuing the reaction for a long time.

It is obvious that the average molecular weight can be reasonably accurately controlled by stopping the reaction at any desired stage. Since the polymers carry unreacted functional groups, they may undergo further condensation on heating. This is undesirable in the technical manipulation of a linear polymer which needs heat for processing, since it may lead to unwanted properties.

This susceptibility to further polymerization can be avoided, and the molecular weight controlled, by the application of the molecular weight stabilization method.[16] This may be accomplished by the addition of a small amount of mono- or bi-functional reactant incorporated in the initial monomers—*e.g.* the polyamides can be stabilized by lauric acid.

If, for example, the reactants are adipic acid and hexamethylene diamine, the polymer will have the structure I, II, or III.

$$\mathrm{H[NH{\cdot}(CH_2)_6{\cdot}NHCO(CH_2)_4{\cdot}CO]_{\mathit{n}}\text{—}OH} \quad . \; . \; . \; . \; . \quad \text{(I)}$$

$$\mathrm{HOOC{\cdot}(CH_2)_4{\cdot}CO[NH(CH_2)_6NHCO(CH_2)_4{\cdot}CO]_{\mathit{n}}\text{—}OH} \quad . \quad \text{(II)}$$

$$\mathrm{H[NH{\cdot}(CH_2)_6{\cdot}NHCO(CH_2)_4{\cdot}CO]_{\mathit{n}}{\cdot}NH(CH_2)_6NH_2} \quad . \; . \quad \text{(III)}$$

In the presence of a fatty acid, $\mathrm{R{\cdot}COOH}$ added to the equimolecular mixture of dibasic acid and diamine, the molecules produced at the completion of amidation will be of three types:

$$\mathrm{R{\cdot}CO[NH(CH_2)_6{\cdot}NHCO(CH_2)_4{\cdot}CO]_{\mathit{n}}\text{—}OH}$$

$$\mathrm{HOOC{\cdot}(CH_2)_4CO[NH(CH_2)_6NHCO(CH_2)_4CO]_{\mathit{n}}\text{—}OH}$$

$$\mathrm{R{\cdot}CO[NH(CH_2)_6NHCO(CH_2)_4CO]_{\mathit{n}-1}{\cdot}NH(CH_2)_6NH{\cdot}COR{\cdot}}$$

and further reaction on heating will be prevented.

Similarly, an excess of one of the reactants in a glycol-dibasic acid condensation will act as a molecular weight stabilizer. Thus, an excess of dibasic acid will stabilize the polymer by formation of

$$\mathrm{HO\text{—}COR'CO[ORO{\cdot}COR'CO]_{\mathit{n}-1}\text{--}OH}$$

The actual relationships of the degree of polymerization to the amount of stabilizer employed and the extent of the reaction have been computed by Flory.[2]

## MOLECULAR SIZE DISTRIBUTION IN LINEAR CONDENSATION POLYMERS

The properties of condensation polymers, composed of a mixture of a wide range of molecular species, will depend not only upon the average molecular weight, but also on the manner in which the different molecular species are distributed about this average. Assuming the principle of equal reactivity of all functional groups, then, as shown by Flory,[17] it is possible to calculate the theoretically probable distribution of molecular species. Consider the general polymerizations of the following types:

*Type 1.* $n(\mathrm{A\text{—}B}) \longrightarrow \mathrm{A\text{—}B(A\text{—}B)_{\mathit{n}-2}A\text{—}B}$

where A and B are functional groups—*e.g.* hydroxyl and carboxyl.

*Type 2.* With two kinds of reactants A—A and B—B (*e.g.* glycol and dibasic acid) three varieties of molecule form in the polymeric mixture, according to whether $n$ is odd or even.

If $n$ is even:

$$\frac{n}{2}\,\text{A—A} + \frac{n}{2}\,\text{B—B} \longrightarrow \text{A—A(B—BA—A)}_{\frac{n-2}{2}}\,\text{B—B}$$

If $n$ is odd:

$$\frac{n+1}{2}\,(\text{A-A}) + \frac{n-1}{2}\,(\text{B—B}) \longrightarrow \text{A-A(B-BA-A)}_{\frac{n-3}{2}}\,\text{B-BA-A}$$

$$\frac{n-1}{2}\,(\text{A-A}) + \frac{n+1}{2}\,(\text{B—B}) \longrightarrow \text{B-BA-A(B-BA-A)}_{\frac{n-3}{2}}\,\text{B-B}$$

To characterize our system we use the following symbols:

$N_0$ = total number of A (or B) groups
$N$ = number of unreacted A (or B) groups remaining at time $t$
$N_0 - N$ = number of reacted A (or B) groups
$p$ = extent of reaction = fraction of total number of A (or B) groups which have reacted at time $t$

$$p = \frac{N_0 - N}{N_0}$$

In reactions of *Type 1*, if A—B is, for example, an hydroxyacid, we may select any monomer unit at random and determine the probability $P_n$ that it is part of a molecule composed of $n$ segments ($n$ mer). Consider a large group of polymerized segments lying end to end

—1———2———3———4———5———6 . . . $n$—

where the numbers denote the linkages between segments; since all unreacted functional groups are equally reactive, the probability that reaction has occurred to link the segments at any particular point is $p$, and the probability that no linkage exists is $1 - p$. In any $n$ mer there are $n - 1$ linkages and two unreacted potential groups; hence the probability that a given monomer unit is at a specified position in the chain of $n$ members is

$$p^{n-1}(1 - p)^2$$

Since there are $n$ possible positions of the chosen monomer unit in the chain of $n$ members, which fulfil the condition that it is part of the $n$ mer, the probability that any $n$ configuration exists is

$$P_n = n \,.\, p^{n-1}(1 - p)^2$$

This probability is proportional to the fraction of the substance actually bound in the $n$ meric chain and, by definition,

$$P_n = \frac{\textit{total no. of segments which exist as components of n mers}}{\textit{total no. of segments}}$$

If, in the condensation process, no molecule of water were eliminated, the molecular weight would be exactly proportional to the number of segments in the molecule, and $P_n$ would exactly equal the weight fraction of $n$ mers ($w_n$). The water actually eliminated causes negligible error except for low molecular weight products.

It follows directly that the number of $n$ mer molecules is given by

$$N_n = \frac{N_0 P_n}{n} = N_0 p^{n-1}(1 - p)^2$$

The total number of molecules of all sizes

$$= \sum_{n=1}^{n=\infty} N_n = N_0(1 - p)^2 \sum_{n=1}^{n=\infty} p^{n-1} = N_0(1 - p)$$

The mol fraction, $\Pi_n$, of $n$ meric molecules is given by

$$\Pi_n = \frac{N_n}{N_0(1 - p)} = p^{n-1}(1 - p)$$

The mol fraction and weight distribution curves calculated from the above equations are shown in *Figures 5* and *6* for various values of $p$.

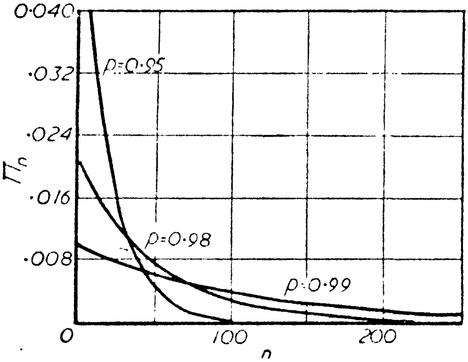


*Figure 5. Molecular weight distribution for linear condensation polymers on a number basis for several extents of reaction p. Mol fractions $\Pi_n$ versus number of structural units n*
(*Reference* : 17)

It is evident from the mol fraction curves that monomers are present to a greater extent than any other species throughout the whole of the reaction. On a weight basis, however, the monomer is in excess only for values of $p < 0{\cdot}5$. The maximum in the distribution curve is sharp for relatively low extents of polymerization, but becomes much broader for large $p$ when more species are present. The actual values of $n$ corresponding to the maximum in $P_n$ can be evaluated directly from the above equation for $P_n$ by setting $\frac{dP_n}{dn} = 0$.

The same molecular weight distribution law applies also to *Type 2* reactions when the numbers of A—A and B—B groups are exactly equal. Mathematical expressions have been derived for the case when one compound is in excess[17], but they are relatively complex.

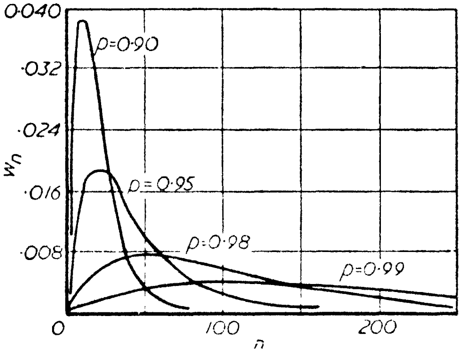


*Figure 6. Molecular weight distribution for linear condensation polymers on a weight basis for several extents of reaction p*
(*Reference* : 17)

*Molecular Weight Averages*—The various average molecular weights can be readily found from the above expressions. The number average molecular weight obtained by chemical end-group determinations or by osmotic pressure measurements (Chapter 5) is given by

$$\bar{m}_n = \frac{\sum_{n=1}^{n=\infty} m_n N_n}{\sum_{n=1}^{n=\infty} N_n}$$

where $m_n$ is the molecular weight of an $n$ mer and $N_n$ is the number of $n$ mers.

Substituting for $m_n$ and $N_n$

$$\bar{m}_n = \frac{m_0 \Sigma n p^{n-1}(1-p)^2}{\Sigma p^{n-1}(1-p)^2}$$

where $m_0$ = molecular weight of a structural unit. The summations are equal, respectively, to 1 and $1-p$, hence

$$\bar{m}_n = \frac{m_0}{1-p}$$

The molecular weight derived by melt or solution viscosities measurements is a weight average molecular weight, defined as

$$\bar{m}_w = \frac{\Sigma m_n w_n}{\Sigma w_n}$$

$$= \frac{\Sigma n m_0 \,.\, n p^{n-1}(1-p)^2}{\Sigma n p^{n-1}(1-p)^2}$$

which, on substituting the values of the summations, $1+p$ and $1-p$ respectively, reduces to

$$\bar{m}_w = m_0 \frac{1+p}{1-p}$$

For high conversions, when $p$ is close to unity, then $\bar{m}_w = 2\bar{m}_n$.

## BRANCHED AND CROSS LINKED POLYMERS

When we consider the more complicated reactions of multifunctional reactants giving rise to three-dimensional structures, the analysis of constitution and molecular weight distribution becomes a much more difficult process. As stated previously, these systems undergo a sudden transformation from a viscous liquid to an elastic gel (of very high viscosity) at a definite stage of the reaction, which is known as the gel point. This change has been attributed to the formation of an infinite network structure,[18] in which a molecular structure of macroscopic size extends through the system. This may be illustrated very clearly by developing a general equation relating the extent of reaction, degree of polymerization and functionality, $f$.

If $N_0$ = the number of monomers initially present
$N_0 f$ = number of functional groups initially present
$N$ = number of molecules after reaction

then $2(N_0 - N)$ = number of functional groups lost

$$\frac{2(N_0 - N)}{N_0 f} = p = \text{extent of reaction}$$

and

$$\frac{N_0}{N} = \text{average degree of polymerization, } \gamma$$

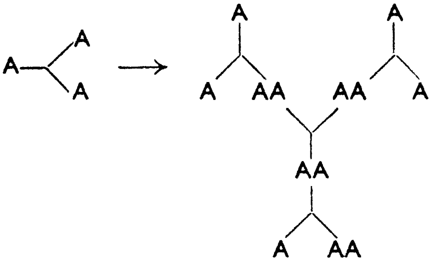
Hence

$$p = \frac{2}{f} - \frac{2}{\gamma f}$$

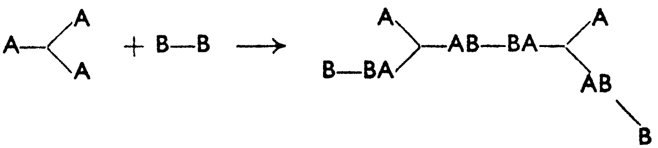
This equation has interesting applications to polyfunctional reactions. For instance, if $\gamma$ is large, the second term can be neglected and $p = \frac{2}{f}$. This determines at what degree of reaction the molecular weight is very large and where, in polyfunctional reactions, gelation occurs and intermolecular reaction ceases. For a reaction between trifunctional molecules, $f = 3$ and $p = \frac{2}{f} = \frac{2}{3}$: it follows that when intermolecular reaction has reached the point where two-thirds of the functional groups have reacted, all units will be combined in a giant molecule. Further reaction takes place intramolecularly. It may also be noted that when $\gamma = 100$, $p = 0{\cdot}660$; thus the average molecular weight will suddenly change from a relatively small to an enormous value over small extents of reaction. Gelation therefore appears suddenly, and experiment has shown that immediately following the gel point a small fraction of the material becomes insoluble in normal solvents, although most of it is soluble and can be extracted. These are differentiated as 'gel' and 'sol' fractions respectively. As condensation polymerization proceeds beyond the gel point, the percentage of gel increases at the expense of the sol, and the polymer at the same time becomes tougher and less extensible.

The exceptional properties of the mixture at the gel point have been shown very clearly in the experiments of KIENLE and collaborators [7] using glycerol and dibasic acids. The average degree of polymerization immediately before gelation commences is very low, but the gel form which appears corresponds to an 'infinite' network.

The statistical method, as applied to linear polymers, has been developed by FLORY [19] and STOCKMAYER [20] to provide quantitative relationships governing the location of the gel point, the change sol ⟶ gel and the molecular size distribution curves. These phenomena are shown to be a direct consequence of the polyfunctionality of the reacting monomer units. The essential features of the problem can be seen by considering the simplest of these systems, that of the condensation polymerization of a trifunctional monomer I or a trifunctional and bifunctional monomer II.



*etc* I

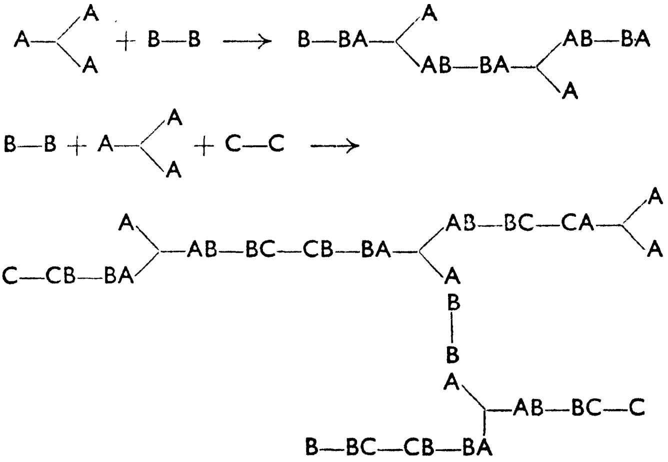


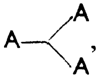
*etc* II

A—A + B—B ⟶ A—AB—BA—AB—BA—A III

In contrast to the linear condensation polymer III, which possesses only two end groups independent of its size, the number of end groups in the case of trifunctional or higher systems increases with increase in size of the molecule. Thus, with the simple trifunctional polymer, polymerization to the trimer gives five as the number of end groups, to the tetramer six end groups, and so on. Generalizing, an *n* mer has $(n + 2)$ end groups, since it contains $3n$ groups in all, of which $2(n - 1)$ have been used to form bonds. The larger molecules, by virtue of their increased number of end groups, have therefore a greater chance of growing than have smaller molecules.

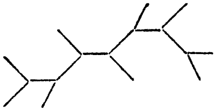
*Gel Point*—Let us consider the formation of a three-dimensional polymer by the condensation of a trifunctional and a bifunctional unit or by reaction of three components, one of which is trifunctional and the other two bifunctional; for instance, the reactions of glycerol and phthalic acid or glycerol, ethylene glycol and succinic acid. These may be represented generally by the equations



where  , B—B, and C—C represent reactants with similar functional groups and AB, AC, and BC are the products of the reactions of two functional groups.

These structures can be regarded as an assembly of chains connected together through trifunctional units, each portion of the molecule between two trifunctional units or between a branch and a terminal unit (unreacted OH or COOH groups) being called a chain. The chains will, of course, be of variable length, and assuming that all the functional groups are equally reactive, a network molecule containing *x* branches possesses $2x + 1$ chains. We are interested in the general condition which will make such an ' infinitely ' large structure possible.

In carrying out this calculation it will be necessary to determine a branching coefficient $\alpha$, which is defined as the probability that one branch will be connected to another branched unit *via* a chain rather than to a terminal group. It is obvious that $\alpha$ will depend on the ratio of the types of reactants and the extent of reaction of the functional groups, and it is possible to see, in a very simple manner, that there exists a critical value of $\alpha$ for which the formation of infinite networks becomes possible. If a chain (variable length) is represented by a straight line as in the following diagram



it is seen that each chain terminating in a branched (trifunctional) unit may be succeeded by two more chains. If both of these terminate in branched units, two more chains are formed, and so on. Thus, if $\alpha < \frac{1}{2}$, there is less than an even chance that each chain will lead to a branched unit, and thus give rise to two more chains; there is greater than an even chance that it will end at an unreacted functional group. In these circumstances the network cannot grow indefinitely. Therefore when $\alpha < \frac{1}{2}$, the structures formed will be finite in size; when $\alpha \gg \frac{1}{2}$, each chain has a chance of producing two new chains and the number of chains will increase during each successive period of growth. Under these conditions branching of chains will continue and an infinite network may be built up. Hence the critical condition for the formation of infinite networks is $\alpha = \frac{1}{2}$.

In our treatment of linear polymers it was assumed that condensation reactions only occur between functional groups on different molecules. This assumption is probably justified, since the opportunities for intramolecular condensation with long chains are very small. This approximation will be less valid in the case of a network structure, since, as a consequence of the increase in the number of functional groups, in the three-dimensional polymer with increase in size, intramolecular linkages will be formed, and will become more abundant as the reaction progresses.

These semi-quantitative results have been deduced by rigorous mathematical methods due to FLORY,[19] who has also generalized the treatment to include polymerization in which branched units of functionality higher than three are present. If the branches are tetrafunctional, then each chain that ends in a branch can give rise to three new chains. By the same reasoning as that in the trifunctional case above, it may be seen that $\alpha$ must exceed $\frac{1}{3}$ for infinite networks to be possible. Generalizing this argument to molecules containing branching units of functionality $f(f > 2)$, infinite networks will be possible when $\alpha(f - 1) \geqslant 1$. The critical value of $\alpha$ therefore is

$$\alpha_c = \frac{1}{f - 1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The sudden transformation of the reaction mixture, during the polymerization of multifunctional reactants, from a viscous liquid to an elastic material of very high viscosity at the gel point has been attributed to the formation of infinite networks. If this is so, the observed gel point should be located at the point at which $\alpha$ reaches the critical value given by equation (6). Experimental results with a number of systems confirm this theory. KIENLE and his coworkers[21] have determined the gel points for a series of polyesters derived by reaction of equivalent amounts of glycerol and a series of dibasic acids (phthalic, succinic, adipic, and sebacic acids). In all cases gelation occurs when the esterified fraction is 76·5–79·5 per cent (*Table VIII*).

*Table VIII*

*Polycondensation of Equivalent Quantities of Glycerol and Phthalic Anhydride*

| *Temperature, °C* | *Time to gel (min)* | *Fraction esterified* |
|---|---|---|
| 160 | 860 | 0·795 |
| 185 | 255 | 0·796 |
| 200 | 105 | 0·796 |
| 215 | 50 | 0·795 |

In the reaction of equivalent amounts of hydroxyl (neglecting any difference in the reactivities of the separate hydroxyl groups in the glycerol) and carboxyl groups, $\alpha = p_{OH}p_{COOH}$, since each connection between branched units requires two ester linkages. $p_{OH}$ and $p_{COOH}$ are the reacted fractions of hydroxyl and carboxyl as previously defined.

In the above experiments, $p_{OH} = p_{COOH}$, and assuming the critical condition, $\alpha = \frac{1}{2}$, the theoretical fraction esterified at the gel point should be $p_c = 0{\cdot}707$, compared with the experimental value of 0·796. The gelation occurs therefore beyond the predicted critical extent of reaction, but this may be due to slight intramolecular condensation.

Similar results for the reaction of diethylene glycol with succinic and adipic acid in the presence of the tribasic tricarballylic acid[22] are summarized in *Table IX*.

*Table IX*

| *Diethylene glycol plus* | $\frac{\text{COOH}}{\text{OH}}$ | *Extent of reaction at gel point* |  | $\alpha_c$ *observed (calc.* 0·50) |
|---|---|---|---|---|
|  |  | *Observed* | *Calc.* |  |
| *Adipic acid* . . | 1·000 | 0·911 | 0·879 | 0·59 |
| *Succinic acid* . . | 1·000 | 0·939 | 0·916 | 0·59 |
| *Succinic acid* . . | 1·000 | 0·894 | 0·843 | 0·62 |
| *Adipic acid* . . | 0·800 | 0·991 | 0·955 | 0·58 |

It thus appears that the agreement between the calculated and experimental values of $\alpha_c$ are sufficiently close to justify the theory of Flory that gelation is caused by the formation of infinite networks.

*Molecular Weight Distribution in Three-dimensional Polymers*—The size distribution for tri- and tetra-functional polymers has been derived by FLORY[19] from probability considerations, and STOCKMAYER[20] has generalized the results to units of any functionality, $f$. The statistical derivation of these relationships will not be repeated here, but the general nature of the results can be arrived at by analogy with the size distribution for the linear chain.

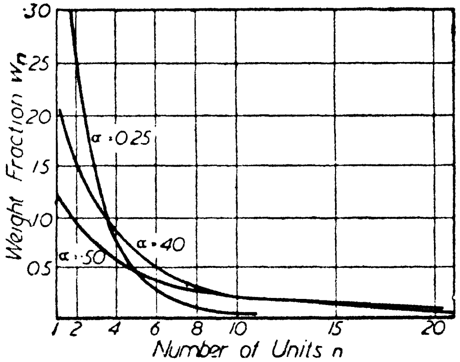


*Figure 7. Molecular size distribution in a three-dimensional polymer. Polymers formed from trifunctional units at various stages of the condensation as indicated by* $\alpha$ ( $= p$). *Weight fraction versus number of units n*

(*Reference* : 2)

For the trifunctional case, an $n$ mer will have $(n - 1)$ bonds, and so $w_n$, defined as in the case of bifunctional molecules, will contain a factor $p^{n-1}$ and also a factor $(1 - p)^{n+2}$, since there are $(n + 2)$ end groups. Since structural isomerism occurs when $n \geqslant 3$, the simple term $n$ is replaced by a more complex expression, which takes this into account. The actual distribution law for $f = 3$ is

$$w_n = \frac{3\,.\,(2n!)}{(n-1)!\,(n+2)!}\,p^{n-1}(1-p)^{n+2} \quad . \quad . \quad . \quad (7)$$

where $w_n$ is the weight fraction of molecules of $n$ units.

For a simple three-dimensional polymerization between trifunctional groups, for instance equal amounts of glycerol and a tribasic acid, the probability, $\alpha$, that one branched unit connects to another is equal to $p_{\mathrm{OH}}(=p_{\mathrm{COOH}})$, since a connection requires one ester linkage. *Figure 7* shows the distribution curves calculated by use of equation (7) for various values of $p = \alpha$. In contrast to the corresponding diagram for linear polymers (*Figure 6*) the curves show a continuous decrease with increase in size of *n*—*i.e.* monomers are always present in a greater amount than any *n* mer. *n* mers are more abundant than $(n + 1)$ mers, *etc.*

At the gel point, $\alpha = 0{\cdot}50$, the curves still show a continuous decrease with *n* and tend to approach 0 as *n* approaches infinity. Even now, the most prevalent type present is the monomer, and the distribution becomes increasingly broad as the extent of polymerization increases. The change of constitution of the polymer as reaction progresses can be shown in a more striking way by plotting weight fractions of various polymers against extent of reaction, $p = \alpha$ (*Figure 8*). It will be seen that $w_1$ decreases continuously as condensation progresses; dimer formation, $w_2$, reaches a maximum near $p = 0{\cdot}2$ and then decreases. The maximum in the formation of the higher polymers occurs at a later stage of the reaction, but in no case does this maximum occur beyond the gel point $\alpha = \frac{1}{2}$.

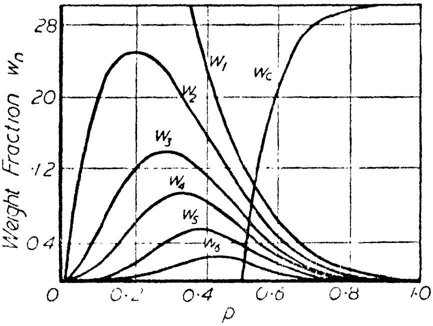


*Figure 8. Weight fractions of various species in a trifunctional condensation as a function of* $\alpha$, *which in this case equals the extent of reaction p.* $w_c$ *is the weight fraction of the gel.* (*Reference* : 2)

*Molecular Weight Averages with Three-Dimensional Polymers*—The average molecular weights may be derived in the following manner. If the number of functional groups per monomer is *f*, then, since two groups react to form each bond, the total number of bonds formed is $\frac{fN_0p}{2}$, where $N_0$ = total number of monomer units. The number of molecules, *N*, is equal to the original number less the number of linkages—*i.e.*

$$N = N_o - \frac{fN_o p}{2}$$

and the average molecular weight $= \overline{m}_n = \frac{N_o}{N} = \frac{1}{(1 - fp/2)}$ (8)

The weight average molecular weight $= \bar{m}_w = \sum_{n=1}^{\infty} m_n w_n / \sum_{n=1}^{\infty} w_n$. The summation, using the values of $w_n$ from equation (7), has been carried out by Stockmayer and leads to the result

$$\bar{m}_w = \frac{1+p}{1-(f-1)p} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (9)$$

According to this result, $\bar{m}_w$ becomes infinite when

$$1 - (f-1)p = 0$$

This critical value of $p_c = \frac{1}{(f-1)}$ may be identified with the gel point. Only when $p$ exceeds $p_c$ does theory permit the formation of infinite networks. Although $\bar{m}_w$ may be 'infinite' at the gel point $\bar{m}_n$ is still very small. Thus, from equation (8) when $f = 3$, $p = \frac{1}{2}$ at the gel point, and therefore $\bar{m}_n = 4$, *i.e.* about a quarter of the molecules which were present initially. This result is in agreement with experiments, since it has been found that glyceryl phthalate polyesters have cryoscopic molecular weights just prior to the gel point corresponding to between 3 and 4 molecular units.

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## CHAPTER 3

# ADDITION POLYMERIZATION

THE PROCESS OF addition polymerization is a chain reaction in the kinetic as well as the structural sense. It is characteristic of molecules which possess a particular type of reactive double or triple bond. This bond is the site of the initiating reaction, which gives rise to an ' active ' centre which may add on a monomer molecule without loss of activity. The chain grows by successive additions of this type until it becomes stabilized and growth ceases. It is usual to resolve the chain process into the fundamental stages of initiation, propagation and termination. The overall rate of polymerization and the sizes of the polymer molecules formed are determined by the rates of these separate processes, and in formulating the complete mechanism of the polyreaction it is necessary that the nature and kinetics of each of the elementary processes should be specified. It is self-evident that the main points for consideration in this chapter will be the formation and nature of the active molecule, its mechanism of growth and the reactions whereby it loses its activity.

## I

## ELEMENTARY PROCESSES IN FREE RADICAL POLYMERIZATIONS

Olefinic molecules such as styrene, some of its substituted derivatives and vinyl acetate polymerize slowly at ordinary temperatures when in the pure state. Most olefinic molecules which are polymerizable require, however, some form of activation, and this may be supplied by thermal or photochemical agencies or by the use of a suitable catalyst. STAUDINGER [1] first proposed that the chain initiator was a monomer molecule in which the double bond had been opened by suitable activation,*

$$CH_2{=}CHX \longrightarrow \dot{C}H_2{-}\dot{C}HX$$

---

* The symbol of the dot above or at the side of the carbon atom is used to denote the free radical state, *e.g.* $CH_3{-}\dot{C}HX$, $CH_3CO\cdot$

This diradical may then add monomer molecules successively at either end without loss of free radical activity.

$$\dot{C}H_2\text{—}\dot{C}HX + CH_2{=}CHX \longrightarrow \dot{C}H_2\text{—}CHX\text{—}CH_2\text{—}\dot{C}HX$$

This type of growth reaction would require only a small activation energy, and termination may be readily explained by the ultimate union of two monoradicals, or by disproportionation accompanied by hydrogen transfer. The initial formation of the diradical by a thermal reaction requires considerable activation, and the most likely mechanism would be the collision and association of two high-energy molecules according to

$$CH_2{=}CHX + CH_2{=}CHX \longrightarrow \cdot CH_2\text{—}CHX\text{—}CH_2\text{—}\dot{C}HX$$

Experiment shows that this type of reaction has an activation energy of the order of 30 kcal, and will thus be infrequent at ordinary temperatures. The diradical state may be formed directly by photoactivation, as has been demonstrated by MELVILLE[2] with vinyl acetate. Photoinitiation is not always such a simple process, and it is often difficult to decide whether the absorbed quantum produces an activated molecule, a diradical, or a monoradical, by dissociation of the monomer. The latter occurs in the photopolymerization of methyl vinyl ketone vapour, the initiation process being the dissociation of the monomer into free radicals (page 47).

In thermal reactions the difficulties of activation at low temperature may be overcome by the use of catalysts, the most efficient being those substances which are known to be reactive towards the double bond. These substances fall into two well defined groups: *a* oxygen, peroxidic compounds, ozonides, free radicals, *etc*; *b* acids, $BF_3$, $SnCl_4$, $TiCl_4$, $AlCl_3$, and other Friedel–Crafts type catalysts. The wide range of properties of these catalysts allows many interpretations of the activating mechanism, but it is broadly agreed that they correspond to the two established types of activation of the double bond: (i) free radical formation by opening of the double bond, as explained above, and (ii) the production of an ionic state $\overset{+}{C}H_2\text{—}\overset{-}{C}HX$ which may be formed by either of the following types of reaction:

$$\overset{+}{Y} + CH_2{=}CHX \longrightarrow YCH_2\text{—}\overset{+}{C}HX$$

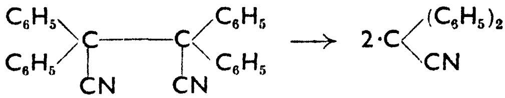
$$R_1R_2 + CH_2{=}CHX \longrightarrow R_1CH_2\text{—}\overset{+}{C}HX + \overset{-}{R}_2$$

It is for this reason that addition polymerizations are broadly classified as determined by either a free radical or an ionic process.

Although most known reactions fall into this classification, it must not be assumed that other types of reaction are precluded.

## FREE RADICAL INITIATION

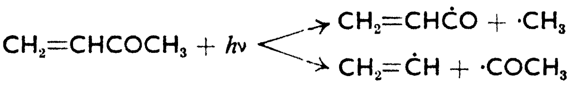
The most striking evidence for the free radical nature of polymerization is obtained by the direct introduction of free radicals into the monomeric system. Thus, triphenyl methyl readily initiates polymerization of styrene in solution.[3] Similarly, the polymerization is accelerated by tetraphenyl succinodinitrile[4] under conditions in which it is known to decompose to give free radicals:



Further, a large number of organic and inorganic compounds which are known to generate free radical intermediates on decomposition are powerful catalysts for polymerization. These compounds include the acyl peroxides, diazonium compounds, persulphates, *etc.* Polymerization may also be initiated by free radicals formed by the photochemical dissociation of added sensitizers. Thus, JONES and MELVILLE[5] have shown that vinyl polymerization may be induced in the vapour phase by the photodecomposition of acetone

$$CH_3COCH_3 \longrightarrow \cdot CH_3 + CH_3CO\cdot \longrightarrow 2\cdot CH_3 + CO$$

or by hydrogen atoms from the mercury sensitized dissociation of hydrogen molecules, and, as previously mentioned, from the photodissociation of the monomer itself, as in the case of methyl vinyl ketone:



$$CH_2{=}CHCOCH_3 + h\nu \begin{cases} \longrightarrow CH_2{=}CH\dot{C}O + \cdot CH_3 \\ \longrightarrow CH_2{=}\dot{C}H + \cdot COCH_3 \end{cases}$$

These radicals initiate polymerization by opening up the double bond of the monomer

$$R\cdot + CH_2{=}CHX \longrightarrow RCH_2{-}\dot{C}HX$$

to form a new radical capable of further growth. It must not be assumed that the introduction of free radicals into the monomer will automatically initiate polymerization and that the process is free of activation energy. Methyl radicals formed by the thermal decomposition of silver methyl at low temperatures (− 60° to −20°C) do not induce polymerization of styrene or acrylonitrile in alcohol solution.[6] These radical addition reactions may require a small activation energy, as may be seen from the following qualitative picture of the reaction. In approaching the double bond the radical may be visualized as drawing out an electron from the electron cloud of the double bond, and this will be dependent on the electron affinity of the radical. This process entails the breaking down of the coupling between the $\pi$ electrons of the double bond, and although the final result of the formation of a homopolar bond leads to energy liberation, the addition reaction may need a small activation energy. Furthermore, the replacement of the hydrogen on the double bond by hydrocarbon or polar groups may, by virtue of their shielding effect, increase the difficulty of reaction. This is in agreement with experimental facts, since the gas-phase polymerization of propylene induced by free methyl radicals is more difficult than the corresponding reaction of ethylene. Symmetrical substitution of the hydrogens of the double bond (with the exception of substitution by fluorine) inhibits polymerization entirely, due principally to stereochemical causes.

If free radical initiation is due to the direct addition of the radical to one end of the double bond, then it is to be expected that the radical would be attached to at least one end of the chain of the polymer. The presence of such end fragments of the catalyst has been confirmed for many types of free radical polymerizations and with several monomers. Benzoyl peroxide decomposes readily in solution at 70–100°C into free phenyl and benzoate radicals[7] according to

$$C_6H_5COO{-}OOCC_6H_5 \longrightarrow C_6H_5COO\cdot + C_6H_5COO\cdot$$
$$C_6H_5COO\cdot \longrightarrow C_6H_5\cdot + CO_2$$

Substituted benzoyl peroxides behave in a similar manner. The presence of these radicals in polystyrene, polymethylmethacrylate, and polyacrylonitrile has been demonstrated by PRICE and his collaborators[8] by the use of anisoyl (I), *p*-bromobenzoyl (II), and 3 : 4 : 5-tribromobenzoyl (III) peroxides. The isolation of *p*-bromobenzoic acid by saponification of the polymer sample prepared using catalyst (II) provides very convincing evidence that the alkoxyl radicals are present in the polymer. Numerous other examples of the detection and quantitative estimation of labelled radicals at the end of polymer chains have been reported.[9] They provide overwhelming evidence that many of the established polymerization catalysts are effective as free radical sources for the activation of the double bond. In many cases the analytical data show the presence of catalyst fragments at one or both ends of the polymer chain. As with condensation polymers, these end group determinations have been used for the measurement of average molecular weights,[10] and values obtained in this way have been shown to be in reasonable agreement with those determined by other methods. In view of the complex nature of the decomposition of peroxides and similar catalysts, together with the analytical difficulties in the accurate determination of end groups on long chains, the method is limited at present, as a quantitative tool, to just a few cases where the exact nature of the kinetics has been established.

The chemical evidence for free radical initiation is strongly supported by kinetic measurements of the rate of catalysed polymerizations. The observed law of the dependence of the consumption of monomer on the concentration of the catalyst may be interpreted simply in terms of a free radical chain. This is discussed in detail later in this chapter.

### PROPAGATION PROCESS

The nature of the propagation process presents little difficulty, since the experimental facts show that a polymerizable monomer, once activated to the free radical state, can add further monomer molecules fairly easily. The normal chain growth may be represented by the successive series of reactions

$$M_1^* + M \longrightarrow M_2^*$$

$$M_2^* + M \longrightarrow M_3^*$$

$$M_n^* + M \longrightarrow M_{n+1}^*$$

The average lifetime $\tau$ of the growing chain has been measured directly in certain photoinitiated polymerizations (page 73). For example, in the gas phase polymerization of vinyl acetate, vinyl chloride, or methyl acrylate, and the liquid phase polymerization of vinyl acetate or styrene, $\tau$ has a value of $10^{-3}$ to $10^{-2}$ sec for a chain length of about 1,000 molecules. In these reactions, polymerization ceases within a small fraction of a second of the cutting off of the light, but in other gas phase polymerizations MELVILLE[11] has shown that a dark reaction continues for long periods—weeks, in some instances—after the photopolymerization. Chloroprene and methyl methacrylate show this phenomenon, and growth occurs in the solid phase of the polymer deposited on the walls of the reaction vessel. How the activity is maintained is not clear. Whatever its nature, the activity of methacrylate is readily destroyed by hydrogen atoms and iodine molecules, and that of chloroprene by oxygen. The interesting fact about the monomers which give these long lived molecules is that they may be made to polymerize in the normal manner without exhibiting these exceptional properties. It appears that one and the same monomer may polymerize in a variety of ways.

## TERMINATION REACTION

In a radical polymerization it is difficult to imagine any type of termination reaction other than that occurring between a pair of radicals. The possibility of ring formation between the growing ends of a diradical chain is so improbable that this type of reaction may be excluded. The principal types of termination reaction are therefore:

*a* reaction of the free radical end of one chain with a similar grouping in another chain
*b* addition of initiator (radical) to the active chain end
*c* termination by impurities such as oxygen, inhibitors, *etc.*

It is not easy to decide which is the predominant mechanism except in special cases, but extensive kinetic studies (page 65) have shown that the most general termination reaction is bimolecular and probably of type *a*. Two such types of bimolecular termination occur:

*1* The union of the radicals by a coupling or combination mechanism

$$R{-}CH_2\dot{C}HX + R{-}CH_2\dot{C}HX \longrightarrow R{-}CH_2CHX{-}CHXCH_2{-}R$$

*2* The transfer of a hydrogen atom, giving a saturated molecule together with the formation of a molecule having an unsaturated terminal group, by a disproportionation mechanism

$$R{-}CH_2\dot{C}HX + R{-}CH_2\dot{C}HX \longrightarrow R{-}CH_2CH_2X + R{-}CH{=}CHX$$

A distinction between these two reactions is possible experimentally if it can be established accurately that the polymer molecule contains one or two catalyst fragments or that half the molecules have unsaturated end groups. Further, the disproportionation mechanism would lead to a lower average molecular weight than the combination mechanism, and this would be reflected in the size distribution curves for the two types of reaction (page 78). From a detailed examination of the polymerization of methyl methacrylate initiated by hydroxyl radicals, BAXENDALE and EVANS [12] have shown that the combination mechanism *1* is the correct one, and that each chain possesses two end-hydroxyl groups.

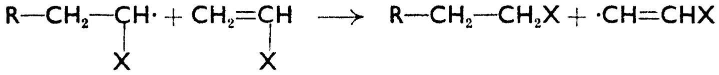
## CHAIN TRANSFER

In addition to the normal chain growth processes, the activity may be transferred from the growing polymer to monomer (M) or solvent (S) molecules :

$$M_n^* + M \longrightarrow M_n + M^*$$
$$M_n^* + S \longrightarrow M_n + S^*$$

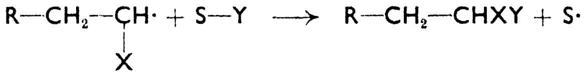
This concept was first introduced by Flory,[13] and is termed chain transfer. It does not destroy the growth process, but decreases the average degree of polymerization. Typical chain transfer processes are :

*a* Chain transfer with monomer



$$R{-}CH_2{-}\underset{X}{CH}\cdot + CH_2{=}\underset{X}{CH} \longrightarrow R{-}CH_2{-}CH_2X + \cdot CH{=}CHX$$

*b* Chain transfer with solvent



$$R{-}CH_2{-}\underset{X}{CH}\cdot + S{-}Y \longrightarrow R{-}CH_2{-}CHXY + S\cdot$$

In both processes the chain is stabilized by the transfer of a monovalent atom from either the monomer or the solvent, and liberates a new radical which may continue the chain. The new chain, if derived from the monomer, would not contain any catalyst fragment. If, however, it is initiated by solvent transfer (process *b*), the chain would contain fragments of the solvent molecule. The latter process has been established for polymerization in halogenated solvents. Breitenbach and Maschin[14] have shown that in the polymerization of styrene in carbon tetrachloride, transfer with the solvent occurs very easily and that each polymer molecule contains fragments of the carbon tetrachloride

$$M_n\cdot + CCl_4 \longrightarrow M_nCl + \cdot CCl_3$$
$$\cdot CCl_3 + M \longrightarrow MCCl_3\cdot \longrightarrow M_nCCl_3\cdot$$
$$M_nCCl_3\cdot + CCl_4 \longrightarrow ClM_n{-}CCl_3 + \cdot CCl_3$$

The occurrence of the transfer of activity does not greatly affect the overall rate of polymerization, since the active centre is maintained, but in the above instance the average molecular weight is considerably reduced. If, in the solvent transfer process, the new radical S· does not react with the monomer and is not effective in propagating the chain, then these radicals will destroy one another by dimerization and the solvent may be looked upon as an inhibitor.

In common with the more familiar chain reactions, addition polyreactions are susceptible to catalysis and inhibition. The existence of an induction period was noted in many of the early investigations of polymerization. This was attributed to the gradual building up of the chain reaction to a steady state. Whilst this building up process must occur and is important kinetically, as shown by Flory [13] and by Nozaki and Bartlett,[15] the presence of variable induction periods in many of the early studies was certainly due to the presence of impurities in the monomer. It is now well established that the addition of very small amounts of substances to the monomer will inhibit polymerization for long, but well defined periods of time, after which the reaction follows its normal course. In fact, one of the major problems in addition polymerization studies is the purification of the monomer from small traces of inhibitor (or in some cases positive catalysts). Studies, both qualitative and quantitative, on the artificially produced induction period have provided a powerful means of investigating the initiation and termination reactions.[2, 75]

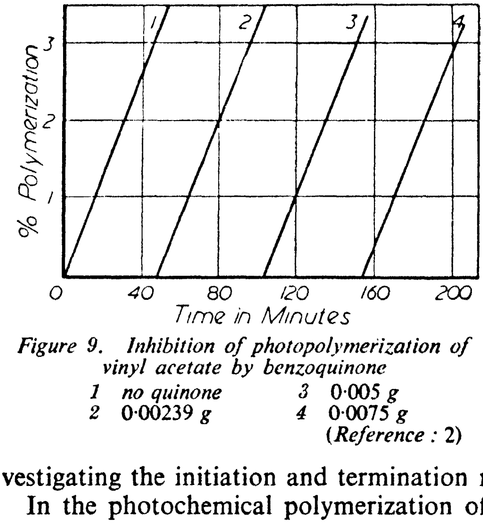


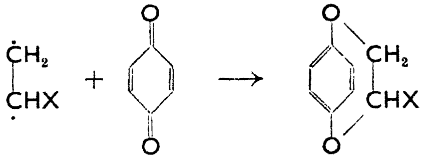
*Figure 9. Inhibition of photopolymerization of vinyl acetate by benzoquinone*

*1* *no quinone* *3* 0·005 *g*
*2* 0·00239 *g* *4* 0·0075 *g*
(*Reference* : 2)

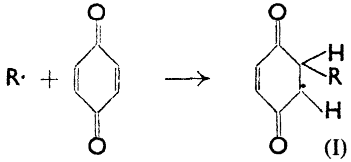
In the photochemical polymerization of vinyl acetate which has been investigated in a very complete manner by Melville and his collaborators,[2] the amount of polymerization as a function of time is accurately linear over a considerable range. In the presence of a small amount of inhibitor—benzoquinone—a well defined induction period appears, after which the rate is precisely identical with that of the uninhibited reaction. Simultaneously, the colour of the quinone is destroyed. The induction period is accurately proportional to the amount of benzoquinone added (*Figure 9*), and it is inferred that each molecule of photochemically activated vinyl acetate reacts chemically with one molecule of quinone. The rate of removal of quinone therefore measures the rate at which the vinyl molecules are activated, and hence the rate of the initiation process may be determined.

Similar observations were made initially by Foord[16] on the inhibition of the polymerization of styrene. From some 130 organic compounds tested as inhibitors, he found that the quinones were the most effective agents. Foord also observed that many organic substances, when present in small amounts, caused a marked decrease in the rate of polymerization, although not inhibiting the reaction at any stage. These substances are known as polymerization 'retarders', and, in contrast to true inhibitors, do not destroy the active centres produced in the initiation process, but deactivate the reactive entities at some stage in the growth process. They function by reducing the chain length and hence the molecular weight of the polymer. The most effective molecules as retarders in vinyl polymerizations are the aromatic nitro-compounds.

The detailed chemistry of inhibitor and retarder action is not known. It may be assumed that benzoquinone can react with and destroy a diradical in the following way

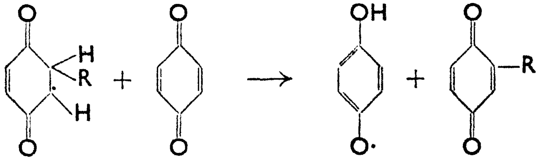


A different mechanism is necessary, however, to explain inhibitor and retarder action with monoradical initiation. Price[17] assumes that the quinone competes for the polymer free radical R·, with the formation of radical (I)



(I)

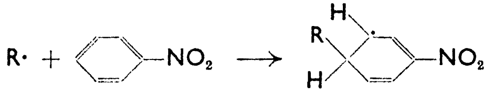
which reacts further with benzoquinone to give a substituted quinone (II) and a quinhydrone-type radical (III)



(I) (III) (II)

The inhibition is assumed to be a result of the stability of the radical (III). This is strongly supported by the independent evidence of EVANS,[18] who has found that semiquinone radicals will not initiate polymerization in aqueous solutions of acrylonitrile and other monomers. The radical (III) eventually undergoes a disproportionation reaction to quinone and hydroquinone. The formation of hydroquinone in styrene inhibited by quinone has been demonstrated experimentally.[19]

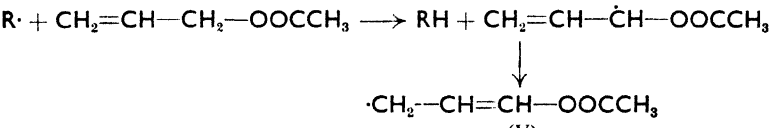
The action of aromatic nitrocompounds as retarders is similar to that of benzoquinone, in that they form with the growing radical a relatively stable radical which will no longer add on monomer units



(IV)

The radical (IV) is stabilized by resonance, and this is in agreement with the well known effect of nitrogroups in conferring increased stability on stable free radicals of the Gomberg type. For instance $\cdot C(C_6H_4NO_2)_3$ is much more stable than $\cdot C(C_6H_5)_3$.

A new type of retarder action has recently been proposed by BARTLETT and ALTSCHUL [20] to explain the observed kinetic results for the polymerization of allyl acetate. The chain terminating process is postulated as that of the collision of a growing free radical chain with a monomer molecule, giving rise to a new free radical of greater stability and smaller reactivity than the old one. This radical is unable to continue the polymerization chain and disappears by dimerization or reaction with other radicals. The terminating reaction is assumed to be



$$R\cdot + CH_2{=}CH{-}CH_2{-}OOCCH_3 \longrightarrow RH + CH_2{=}CH{-}\dot{C}H{-}OOCCH_3$$
$$\downarrow$$
$$\cdot CH_2{-}CH{=}CH{-}OOCCH_3$$

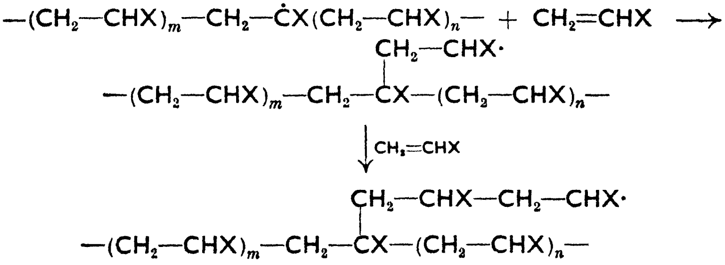
(V)

the radical (V) being stabilized by resonance in such a way as to make it much less reactive than the radical type present as a chain carrier. The authors have named this mode of termination ‘ degradative chain transfer ’.

## BRANCHING, CROSS LINKING, AND DEPOLYMERIZATION

As pointed out by TAYLOR and TOBOLSKY,[21] the principle of microscopic reversibility would lead us to suspect that not only can a growing chain transfer its reactivity to a monomer or a solvent molecule, but an active monomer or other free radical can transfer its activity to an inactive long chain molecule. Furthermore, this activity may be transferred to any position along the chain and not necessarily to the chain ends only.

The presence of an active centre along the chain gives rise to the secondary reactions of branching, cross linking and depolymerization. It is not surprising, therefore, to find a small degree of branched or even cross linked chains in a simple polymer. The formation of branches results when the hydrocarbon radical reacts with a monomer, and this may be represented as follows



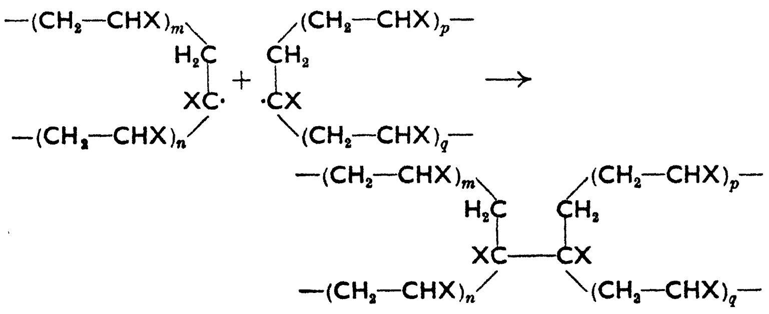
$$-(CH_2-CHX)_m-CH_2-\dot{C}X(CH_2-CHX)_n- + CH_2{=}CHX \longrightarrow$$

$$-(CH_2-CHX)_m-CH_2-\overset{CH_2-CHX\cdot}{\overset{|}{C}}X-(CH_2-CHX)_n-$$

$$\Big\downarrow{\scriptstyle CH_2=CHX}$$

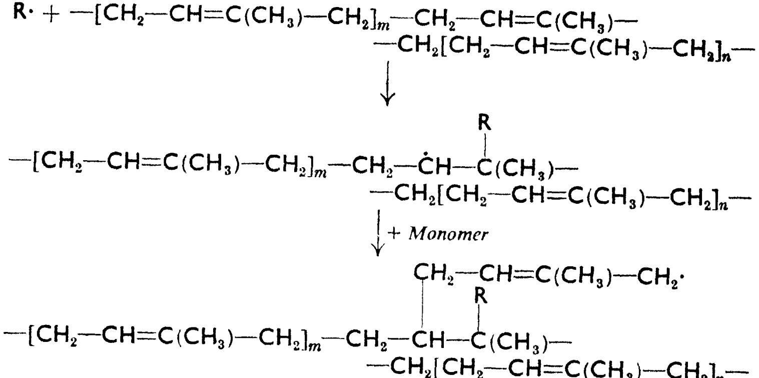
$$-(CH_2-CHX)_m-CH_2-\overset{CH_2-CHX-CH_2-CHX\cdot}{\overset{|}{C}}X-(CH_2-CHX)_n-$$

Cross linking occurs when two radicals combine in the following manner



In view of the steric requirements of this process, the probability of two chains approaching the configuration for combination is very small, and thus cross linking is a very infrequent process.

In the case of diene polymers, branching can occur exactly as with the vinyl polymers; for example



$$\mathrm{R\cdot + {-}[CH_2{-}CH{=}C(CH_3){-}CH_2]_{\mathit{m}}{-}CH_2{-}CH{=}C(CH_3){-}CH_2[CH_2{-}CH{=}C(CH_3){-}CH_2]_{\mathit{n}}{-}}$$

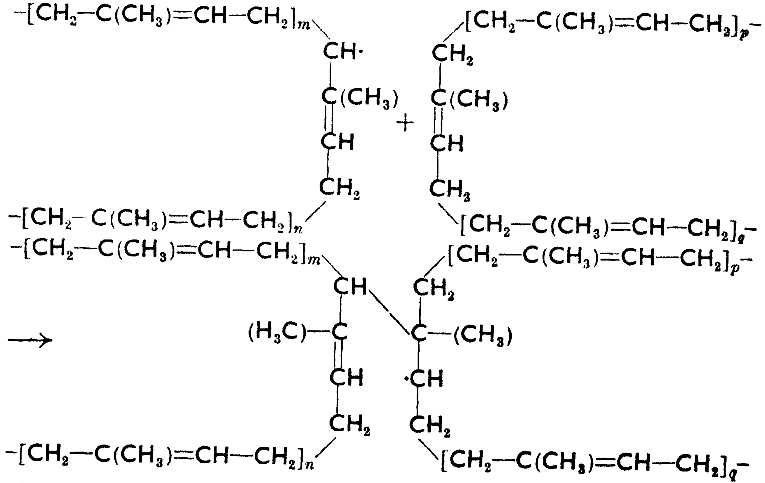
$$\downarrow$$

$$\mathrm{{-}[CH_2{-}CH{=}C(CH_3){-}CH_2]_{\mathit{m}}{-}CH_2{-}\dot{C}H{-}\overset{R}{\overset{|}{C}}(CH_3){-}CH_2[CH_2{-}CH{=}C(CH_3){-}CH_2]_{\mathit{n}}{-}}$$

$$\downarrow + \textit{Monomer}$$

$$\mathrm{{-}[CH_2{-}CH{=}C(CH_3){-}CH_2]_{\mathit{m}}{-}CH_2{-}\overset{CH_2{-}CH{=}C(CH_3){-}CH_2\cdot}{\overset{|}{C}H}{-}\overset{R}{\overset{|}{C}}(CH_3){-}CH_2[CH_2{-}CH{=}C(CH_3){-}CH_2]_{\mathit{n}}{-}}$$

Cross linking can, however, occur much more readily in dienes than in the vinyl polymers, because we now have the additional possibility of reaction of the hydrocarbon radical with the double bond of an adjacent chain.



This is in agreement with the observed tendency of cross linking in diene polymerizations.

By analogy with the disproportionation reaction of free radicals, the depolymerization process

$$\mathrm{{-}(CH_2{-}CHX)_{\mathit{m}}{-}CH_2{-}\dot{C}X{-}(CH_2CHX)_{\mathit{n}}{-} \longrightarrow {-}(CH_2{-}CHX)_{\mathit{m}-1}{-}CH_2{-}CHX\cdot + CH_2{=}CX{-}(CH_2{-}CH_2X)_{\mathit{n}}{-}}$$

may not be difficult energetically. The reaction is the inverse of the polymerization process. The critical splitting can occur at any place along the chain, and this may be followed by a continuous splitting of the radical fragments formed. The depolymerization to monomer units is thus a chain process. The energy of activation for depolymerization may be estimated as being equal to the energy of activation of propagation plus the heat of polymerization, and in vinyl polymers this is about 25 kcal. If the frequency term in the rate expression is normal, depolymerization may occur readily at not too high temperatures. At the higher temperatures, depolymerization may compete with polymerization. TOBOLSKY and MESOBRIAN [22] have shown experimentally that both processes occur when high molecular weight styrene is heated in the presence of a small amount of air at 100°C and that a steady state is reached. These reactions may also be important in the determination of the final distribution of molecular sizes under any given experimental conditions.

## II

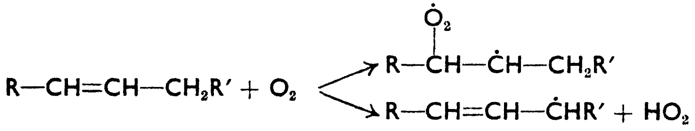
## ROLE OF OXYGEN IN POLYMERIZATIONS

Atmospheric oxygen exerts a very profound influence on many polymerization processes. With many vinyl compounds, oxygen exerts a marked inhibiting effect. Thus, STAUDINGER and his collaborators [23] showed that $O_2$ acted as an inhibitor in the photopolymerization of vinyl acetate, acrylic acid and its esters. This effect can be readily explained if the activated monomer molecules absorb $O_2$

$$\begin{aligned} M + h\nu &\longrightarrow {}^*M^* \\ {}^*M^* + O_2 &\longrightarrow \textit{Peroxide} \end{aligned}$$

with the formation of peroxidic compounds. If this explanation is correct, oxygen effects should be observable with thermal polymerization. STAUDINGER and URICH [24] showed that methyl acrylate heated at 100°C in the absence of air did not polymerize, but when air was admitted polymerization occurred immediately. Similar results confirming these observations were obtained with vinyl acetate, vinyl bromide, and other monomers. In all cases small amounts of benzoyl peroxide induced thermal polymerization. Recently BARNES [25] has examined the nature of the interaction between oxygen and a very large number of vinyl monomers. In all cases he found that oxygen was absorbed, and he showed the presence of peroxides by analysis. It is obvious, therefore, that oxygen can function in two diametrically opposite ways; either *1* it may deactivate chains by the formation of stable peroxides or *2* the peroxides formed may generate free radicals as a result of their thermal instability and thus initiate polymerization. Which course is followed—that is, whether the oxygen is functioning as an inhibitor or activator—depends on a delicate balance between these processes, and thus on the amount and accessibility of the oxygen to the bulk of the polymer and on the temperature. Thus, with an increase in temperature the peroxide builds up, and the resulting increased rate of decomposition generates more active centres than can be destroyed by the oxygen; polymerization therefore ensues. The very pronounced inhibiting effect of oxygen in emulsion and aqueous solution polymerizations will be discussed in a later paragraph. The mechanism of action in these cases is similar, but the marked inhibiting action is due to the fact that emulsion polymerizations are usually studied around room temperature, when peroxidic decomposition is usually unimportant. At high temperatures the inhibition is less noticeable.

*Reaction of Oxygen with Olefinic Systems*—Besides the interaction of oxygen with free radicals, a large amount of experimental evidence shows that oxygen may react directly with an olefinic system, and this is in keeping with the free radical nature of the oxygen molecule. With the simple olefins, $CH_2{=}CR_1R_2$, the oxygen reacts directly with the double bond, but with olefins possessing α-methylene groups or with conjugated and unconjugated olefins of the type $CH_2{=}CH{-}CH{=}CH{-}CH_2{-}$ and $-CH{=}CH{-}CH_2{-}CH{=}CH{-}$, the work of FARMER and his collaborators[26] has shown that the point of oxygen attack is principally at the reactive α-methylene group. The two possible modes of oxygen reaction may be represented as:



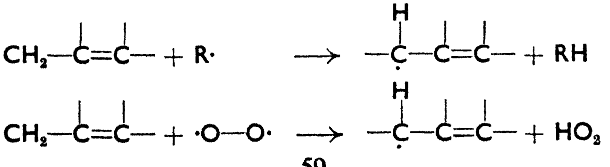
$$\mathrm{R{-}CH{=}CH{-}CH_2R' + O_2} \begin{array}{l} \nearrow \mathrm{R{-}\overset{\dot{O}_2}{\overset{|}{C}}H{-}\dot{C}H{-}CH_2R'} \\ \searrow \mathrm{R{-}CH{=}CH{-}\dot{C}HR' + HO_2} \end{array}$$

These types of reaction are not mutually exclusive, and we should expect both to occur together in many cases, the predominancy of one or the other being determined by their relative rates. It is not our purpose to discuss in detail the secondary oxidation processes which follow the primary reaction of oxygen with the mono- and poly-olefins. This subject has been extensively studied in relation to the oxidative mechanism of the drying of oils and the fission of long chain unsaturated molecules, of which rubber is the most important example. All that we can hope to do is to indicate the main types of reaction of oxygen–olefinic systems as they affect polymerization studies.

In systems where α-methylenic activity is not strongly developed, additive reaction is preferred and, of course, in olefins which contain no α-methylene groups this is the only initiating mechanism. FARMER [27] has shown that for a number of unconjugated olefins the initial products of the autoxidation are hydroperoxides, ROOH, in which the unsaturation of the olefin is preserved. These are unstable molecules, and their rate of decomposition varies with the olefinic structure. Thus the hydroperoxides of cyclohexene, 1-methylcyclohexene, 1 : 2-dimethylcyclohexene, and methyl oleate can be isolated by fractional distillation. In other cases, such as the polyisoprenes *e.g.* dihydromyrcene, $H(CH_2{-}CMe{=}CH{-}CH_2)_2H$, and rubber $(CH_2{-}CMe{=}CH{-}CH_2)_n$, drying-oil acids such as linoleic acid $(C_5H_{11}{-}CH{=}CH{-}CH_2{-}CH{=}CH{-}(CH_2)_7COOH)$ and linolenic acid $(C_2H_5{-}CH{=}CH{-}CH_2{-}CH{=}CH{-}CH_2{-}CH{=}CH{-}(CH_2)_7COOH)$, as well as the unconjugated polyene acids (eicosatetraenoic acid and decosahexaenoic acid), the peroxidic compounds which accumulate in the early stages of oxygen absorption readily decompose or undergo secondary reactions. In addition to α-methylenic hydroperoxide formation, oxidation in many cases leads to stable peroxides of polymeric character. These polymers, however, rarely exceed octamers in complexity and are usually formed together with oxidative fission products. Their structures are very uncertain, but Farmer has shown that the most probable reaction of the conjugated olefin, $CHR{=}CH{-}CH{=}CHR'$, is to form the 1 : 4 interpolymer with oxygen

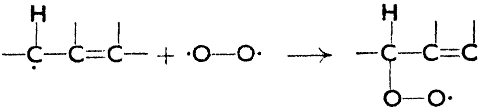
$$-CHR{-}CH{=}CH{-}CHR'OO[CHR{-}CH{=}CH{-}CHR'OO]_n{-}$$
$$-CHR{-}CH{=}CH{-}CHR'OO-$$

He pointed out that the site of attack of free phenyl radicals, produced by decomposition of dibenzoyl peroxide and benzene diazoacetate, was at the methylene group adjacent to the double bond, and suggested that the peroxidation mechanism involved a free radical chain, in which the starting catalyst was a free radical R (including oxygen):



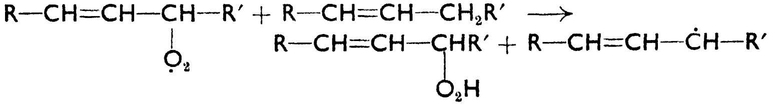
$$CH_2{-}\overset{|}{C}{=}\overset{|}{C}{-} + R\cdot \longrightarrow {-}\underset{\cdot}{\overset{H}{\overset{|}{C}}}{-}\overset{|}{C}{=}\overset{|}{C}{-} + RH$$

$$CH_2{-}\overset{|}{C}{=}\overset{|}{C}{-} + \cdot O{-}O\cdot \longrightarrow {-}\underset{\cdot}{\overset{H}{\overset{|}{C}}}{-}\overset{|}{C}{=}\overset{|}{C}{-} + HO_2$$



$$-\overset{\displaystyle H}{\underset{\cdot}{\overset{|}{C}}}-\overset{|}{C}=\overset{|}{C}-+\cdot O-O\cdot\longrightarrow-\overset{\displaystyle H}{\underset{\underset{\displaystyle O-O\cdot}{|}}{\overset{|}{C}}}-\overset{|}{C}=\overset{|}{C}$$

Hydroperoxides are then formed by detachment of α-methylenic hydrogen from another olefin molecule. For example,

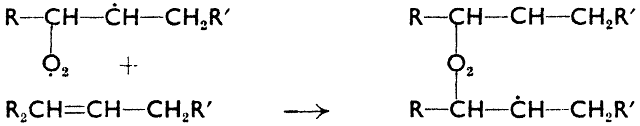


$$R-CH=CH-\underset{\underset{\underset{\cdot}{O}_2}{|}}{CH}-R'+R-CH=CH-CH_2R'\longrightarrow R-CH=CH-\underset{\underset{O_2H}{|}}{C}HR'+R-CH=CH-\dot{C}H-R'$$

Intramolecular reaction by detachment of the hydrogen from an adjacent α-methylene group

$$-CH_2-\dot{C}H-CH_2OO\cdot\longrightarrow-CH=CH-CH_2OOH,$$

is also possible, but reaction does not entirely take place in this way, since it would not lead to propagation of the chains. This scheme also explains satisfactorily the formation of polymeric peroxides. Just as oxygen may attack either a double bond or an active methylene group, so it can be anticipated that a further possible reaction is that of the peroxide radical with a double bond

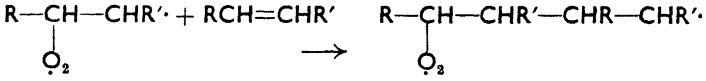
a 

$$\begin{array}{ccc} R-\underset{\underset{\underset{\cdot}{O}_2}{|}}{C}H-\dot{C}H-CH_2R' & & R-\underset{\underset{O_2}{|}}{C}H-CH-CH_2R' \\ + & & \\ R_2CH=CH-CH_2R' & \longrightarrow & R-\overset{|}{C}H-\dot{C}H-CH_2R' \end{array}$$

and, by reaction of the free radical ends with oxygen, a polymeric chain with repeating unit $-CH(CH_2R')-CHR-O_2-$ may be built up. In the case of a conjugated olefin, addition can also take place across the double bond of the terminal carbon atoms, giving

$$-[CHR-CH=CH-CHR'O_2]_n-$$

So far we have assumed that the reaction of the hydrocarbon radical is solely with oxygen. An obvious alternative to this reaction is the addition of the radical at the double bond, giving rise to a typical olefin polymerization

b 

$$R-\underset{\underset{\underset{\cdot}{O}_2}{|}}{C}H-CHR'\cdot+RCH=CHR'\longrightarrow R-\underset{\underset{\underset{\cdot}{O}_2}{|}}{C}H-CHR'-CHR-CHR'\cdot$$

Bolland and Gee[28] have shown that this reaction is 17 kcal exothermic for mono- or 1 : 4-diolefins, and 10 kcal exothermic for 1 : 3-diolefins; hence the reaction would be highly probable, especially at low $O_2$ pressures. In contrast, an $\alpha$-methylenic free radical is much less likely to promote polymerization, since the estimated heats of reaction for addition to the double bond are 2 kcal (mono), 1 kcal (1 : 3), and 6 kcal (1 : 4) endothermic respectively.

Reactions *a* and *b* represent alternative processes leading to polymeric peroxide and hydrocarbon polymers respectively. Both may proceed together, and the nature of the product will be dependent on the conditions of reaction. These possibilities have not been investigated, but MEDVEDEV and ZEITLIN [29] have pointed out the close connection between oxidation and polymerization and have shown that the thermal oxidation of styrene is accompanied by a considerable amount of polymer formation.

*Peroxidic Structure and Chain Fission*—It has already been shown that the secondary reactions of long chain molecules—namely, depolymerization, branching, and cross linking—all involve the presence of an odd electron active centre at some point along the hydrocarbon chain. A very small number of these centres may be present in thermal equilibrium with the hydrocarbon, but probably the majority of these hydrocarbon radicals are formed by the action of oxygen. The oxygen molecules can attack the chain by abstracting a hydrogen atom; for example

$$\text{—(CH}_2\text{—CHX)}_m\text{—CH}_2\text{—CHX(CH}_2\text{CHX)}_n + \text{O}_2 \longrightarrow$$
$$\text{(CH}_2\text{—CHX)}_m\text{CH}_2\dot{\text{C}}\text{X—(CH}_2\text{CHX)}_n\text{—} + \cdot\text{OOH}$$

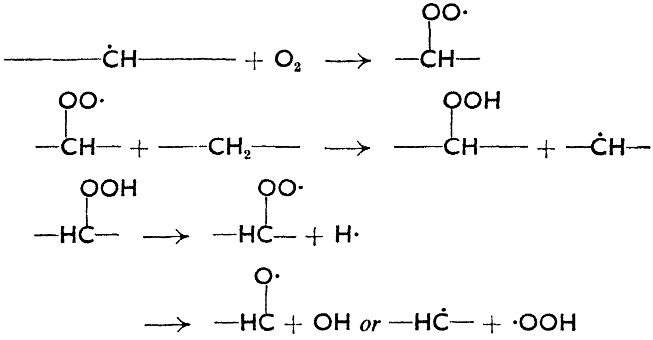
or

$$\text{(CH}_2\text{CX=CHCH}_2\text{)}_m\text{-CH}_2\text{CX=CH-CH}_2\text{-(CH}_2\text{CX=CH-CH}_2\text{)}_n + \text{O}_2 \longrightarrow$$
$$\text{-OOH} + \text{(CH}_2\text{-CX=CH-CH}_2\text{)}_m\dot{\text{C}}\text{H-CX=CH-CH}_2\text{(CH}_2\text{CX=CHCH}_2\text{)}_n\text{-}$$

Chain fission and depolymerization can then occur as previously demonstrated (page 55).

FARMER [30] has postulated that the initial reaction in the oxidation of rubber is the formation of a hydroperoxide on the methylene group alpha to the double bond, which can then undergo various secondary reactions, including attack on the double bond to form cyclic ethers, peroxidic chain fission yielding alcoholic, aldehydic, or carboxylic groups, and peroxidic cross linking. The fundamental role of oxygen seems to be that of producing and maintaining a supply of hydrocarbon free radicals, the reactions of which (fission and cross linking) produce important changes in the physical properties. Oxygen acts as a catalyst, but is chemically combined with the polymer in the process.

*Role of Oxygen in Promoting Branched Chains*—The addition of oxygen to free radicals may produce branched chains which may be represented symbolically in the following manner



$$—\dot{C}H— + O_2 \longrightarrow —\overset{OO\cdot}{\overset{|}{C}}H—$$

$$—\overset{OO\cdot}{\overset{|}{C}}H— + —CH_2— \longrightarrow —\overset{OOH}{\overset{|}{C}}H— + —\dot{C}H—$$

$$—H\overset{OOH}{\overset{|}{C}}— \longrightarrow —H\overset{OO\cdot}{\overset{|}{C}}— + H\cdot$$

$$\longrightarrow —H\overset{O\cdot}{\overset{|}{C}} + OH \text{ or } —H\dot{C}— + \cdot OOH$$

The exact mechanism of the thermal breakdown of the hydroperoxides is still obscure, but the autocatalytic nature of many oxidation reactions indicates that an active radical similar to OH is produced in the primary process. This radical may react further, either at a double bond or by hydrogen extraction from the hydrocarbon chain.

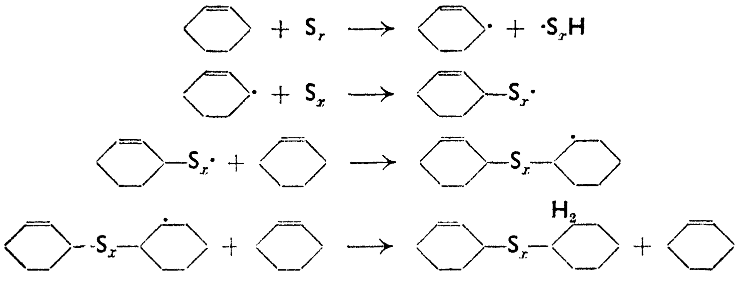
Closely related to the promotion of branching by oxygen is the interesting phenomenon of the photogelation of rubber. When rubber solutions are exposed to ultraviolet light in the absence or in the presence of very limited amounts of oxygen, gelling occurs. The resulting rubber shows the properties of insolubility, swelling, and decrease in plasticity characteristic of cross linked rubber. This close similarity has emphasized the importance of the fundamental study of photogelation as a possible method of elucidation of the nature of vulcanization. The phenomenon has been studied by a number of workers and has recently been comprehensively reviewed by STEVENS[31] and NAUNTON.[32] With certain solvents, such as carbon tetrachloride, elements of the solvent molecule are found in the final rubber. The gelling is accelerated by activators such as aldehydes or ketones. Both of these facts indicate the participation of free radicals in the reaction mechanism, since it is known, first, that in free radical polymerizations in carbon tetrachloride and other halogenated solvents fragments of the solvent are incorporated in the polymer by a typical transfer mechanism (page 51), and secondly, that the photolysis of aldehydes and ketones gives free radicals. This viewpoint is further supported by the observation that well known polymerization inhibitors and antioxygens such as hydroquinone delay gelling. With limited amounts of oxygen, gelling is delayed until all the oxygen is absorbed. This may be explained, either by a reaction causing the removal of free radical centres or, with large amounts of oxygen, by the oxidative disruption of the rubber to such an extent that gelation never occurs. The well known vulcanizing effect of peroxidic compounds has led to the suggestion that oxygen is vital to the photogelation process and is necessary for the initiation of the reaction. All attempts to prevent gelation by removal of oxygen have failed; in fact, the result of careful purification is to reduce the time of gelling. Naunton is, however, of the opinion that gelling is due to oxygenated centres already in the rubber, and that gels result from the formation of oxygen bridges. The unavoidable conclusion from these results is that the reaction is of the chain type, in which the rubber molecules are linked together. The difficulty is to specify the exact nature of the process producing the initial radical. This may be either the direct photolysis of the rubber chain or the production of a free radical from an activator present in minute amounts. The chain reaction leading to cross linkage may be assumed to be of a nature similar to those previously postulated (page 55).

## SULPHUR AND THE OLEFINIC BOND

It is to be expected that sulphur, belonging to the same chemical group as oxygen and having two unpaired electrons in its outer shell, might well behave in a similar manner to oxygen in its attack on the double bond. By analogy, the initial reaction may be

$$-CH_2-CH{=}CH- + S_x \longrightarrow -\dot{C}H-CH{=}CH- + S_xH$$

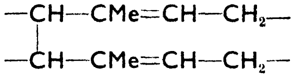
In fact, extensive investigations by FARMER and his collaborators,[33] using both mono-olefins and bi-spaced polyolefins, strongly support this view. The unaccelerated reaction between sulphur and simple mono-olefins leads almost exclusively to cross linking of the separate olefin molecules, mainly in pairs, by groups of sulphur atoms. The products have the composition, $R-S_x-R'$, where R and R′ are radicals derived from the olefin by loss or gain of a hydrogen atom and $x$ varies from 1 to 5 according to the experimental conditions. Thus cyclohexene, $C_6H_{10}$, when heated with sulphur at 140°C, gives a mixture of average composition, $C_6H_9SC_6H_{11}$. Quite similarly, the sulphuration of isobutylene at 140°C gives a product of average composition $CHMe_2-CH_2-S_x-CH_2-CMe{=}CH_2$. The reaction occurs *via* a non-polar mechanism, and attack by sulphur probably occurs at the methylenic hydrogen, the free sulpho radical subsequently formed adding to the double bond of another olefinic molecule; thus



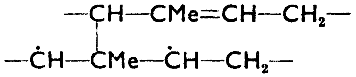
In passing from a mono-olefin to a diolefin the complexity of the reaction increases considerably. The diisoprene–dihydromyrcene gives a mixture of polysulphides strictly comparable with the mono-olefins, together with $R—S_x—R'$ and a cyclic sulphide. Cyclization, in this case, is a special case of cross linking in which sulphur is linked intramolecularly.

The close connection between these sulphuration processes and the vulcanization of natural and synthetic rubbers is obvious. The rubber before vulcanization has a low tensile strength, limited elasticity, and good solubility, but after vulcanization it is transformed into a tough product of high extensive elasticity and it loses the property of solubility; it also shows only limited swelling in suitable solvents. It has been widely assumed that these changes in properties on vulcanization are determined by chemical cross links between polymer molecules. The sulphur vulcanization process as applied to rubber presents many other interesting and elaborate features, especially those connected with auxiliary participators in the process, such as the acceleration of the process by innumerable organic materials.

In view of the formidable nature of the rubber molecule, the chemistry of sulphuration of the simple olefins and other cross linking reactions provides the most direct approach to the unravelling of this complex problem. It has been noted above that the radical sulpho group attached to an olefinic chain may add to the double bond of another molecule. In the case of mono-olefins there is no alternative to this type of intermolecular action, unless the reaction ends in mercaptan formation and the reaction product consists of hydrocarbon molecules cross linked by sulphur. The result is that one of the two original double bonds of the reacting pair of mono-olefin molecules is destroyed and one retained. Farmer has shown that this result is quite a general one for unconjugated olefins, including long chain polyolefins built up from 2 to 6 isoprene units. Since these hydrocarbons in their chemical behaviour show a close resemblance to that of rubber, it may be argued that the properties conferred by the vulcanization of natural rubber are, at least in part, a direct result of the cross linking by sulphur of the macromolecules. The links are probably sulphide or polysulphide bridges; their number is unknown, but need not be very large. This general picture is entirely in line with the well known observations that peroxides and azo compounds, which are known to give radicals on thermal decomposition, are vulcanizing agents for rubber. By analogy with simpler systems, it may be assumed that the free radicals attack the methylene groups, and that the cross linking results either through bonds connecting methylene groups on different rubber molecules or by bonds joining methylene groups to double bonds.



$$\begin{array}{ll} - & \mathrm{CH-CMe{=}CH-CH_2-} \\ & | \\ - & \mathrm{CH-CMe{=}CH-CH_2-} \end{array}$$



$$\begin{array}{llll} & - & \mathrm{CH-CMe{=}CH-CH_2-} & \\ & & | & \\ -\mathrm{\dot{C}H} & - & \mathrm{CMe-\dot{C}H-CH_2-} & \end{array}$$

# III
# GENERAL KINETICS OF FREE RADICAL POLYMERIZATION

The foregoing summary of experimental observations establishes without any question of doubt the free radical mechanism of peroxide-induced and other types of addition polymerization. At present, however, there are very few cases in which a reasonably complete description of all the processes involved in the total polymerization reaction can be given. The ultimate aim of these investigations is to present a detailed chemical and kinetic description of all the elementary reactions occurring. The major difficulty is the number of possible reactions and mechanisms involved, and this makes the mathematical formulation of the kinetic and size distribution relationships one of great difficulty. Much progress has been made towards this goal in recent years, but before we proceed to develop these relationships we shall review firstly the experimental data derived from kinetic studies.

The most thoroughly studied reaction is that of the polymerization of styrene. In the pure liquid monomer the rate of polymerization was formerly assumed to obey a first order law,[34] but the experimental data have recently been more satisfactorily reinterpreted in terms of the second order law [39]

$$-\frac{dM}{dt} = k_0 M^2$$

where $k_0$ = overall velocity constant and $M$ represents the monomer concentration. The same law represents the thermal polymerization, in the absence of any intentional catalyst, in seven different solvents.[35] The rate of consumption of the styrene is not very different in the different solvents, although the mean molecular weight varies greatly. These variations have been shown to be due to chain transfer with the solvent. In the presence of a catalyst, the polymerization occurs faster, and thus the rate can be conveniently measured at lower temperatures; the polymer produced is, however, of lower molecular weight. The initial rate of polymerization of the benzoyl peroxide catalysed reaction in toluene [35a] is accurately represented by the law

$$-\frac{dM}{dt} = k_0 B^{\frac{1}{2}} M^{3/2}$$

where $B$ is concentration of benzoyl peroxide present initially. The average degree of polymerization is inversely proportional to the square root of the benzoyl peroxide concentration. A similar relationship has been found for the benzoyl peroxide catalysed polymerization of vinyl acetate.[36] The rates of polymerization of *l*-β-phenyl butyrate and *d*-*s*.-butyl-α-chloracrylate [37] in dilute solution catalysed by benzoyl peroxide also show a half order dependence on catalyst concentration, but with these two substances the rate is accurately first order with respect to the monomer.

The above results are typical of those attained in a kinetic study of the total polymerization reaction. The measurement of the overall rate of monomer consumption, and the number or weight average degree of polymerization, together with their dependence on catalyst concentration, temperature and solvent, must now be interpreted in terms of the various elementary processes of initiation, propagation, termination, chain transfer, *etc*, which go to make up the complete reaction. In order to do this, we have to make some assumptions regarding the natures of the elementary processes. The possible types of reaction occurring have already been discussed. We now proceed to select a possible scheme, assigning a rate constant to each step and evaluating the kinetic law. If, in this way, the experimentally determined relationship is deduced, then the reasonableness of the speculation as to the assumed mechanism may be accepted. The scheme may be tested and checked by carefully designed experiments.

As an illustration of the general kinetic problem we shall select in the first instance a simple case in which the polymerization is determined by the elementary processes of initiation, propagation, and termination, neglecting such complicating influences as chain transfer, branching, *etc.* Since the propagation process involves only the addition of monomer to the polymer radical, the velocity of propagation is $V_{prop} = k_p M C^*$, where $C^*$ is the total concentration of polymer radicals. Assuming that long chains are formed, the velocity of propagation is much greater than that of termination. The free radical mechanism leads to a termination reaction involving the destruction of radicals in pairs either by the recombination or disproportionation processes. In either case the velocity of termination, $V_{term} = k_t C^{*2}$. The initial activation process may show a first or second order dependence on monomer concentration, or may be determined by collision with a catalyst molecule or by the light absorbed, if the activation is photochemical. These various possibilities will be considered later in this section, but for the present we may assume the general initiation process $\mathrm{M} \rightarrow \mathrm{M}^*$ without specifying its exact nature, and assign to it a velocity constant $k_i$. The total reaction is therefore

$$\begin{array}{lllllll}
 & & & & & \textit{Velocity constant} & \\
\textit{Initiation} & & \mathrm{M} & \longrightarrow & \mathrm{M}_1^* & k_i & .\ .\ (1) \\
\textit{Propagation} & \mathrm{M}_1^* & +\ \mathrm{M} & \longrightarrow & \mathrm{M}_2^* & k_p & .\ .\ (2) \\
 & \mathrm{M}_2^* & +\ \mathrm{M} & \longrightarrow & \mathrm{M}_3^* & k_p & \\
 & \mathrm{M}_{n-1}^* & +\ \mathrm{M} & \longrightarrow & \mathrm{M}_n^* & k_p & \\
\textit{Termination} & \mathrm{M}_n^* & +\ \mathrm{M}_m^* & \longrightarrow & \mathrm{M}_{n+m} & k_t & .\ .\ (3)
\end{array}$$

If it is assumed that the velocity constant of propagation $k_p$ is the same for all steps independent of radical size, it follows that the overall rate of monomer consumption is

$$-\frac{dM}{dt} = V_{init} + V_{prop} = V_{init} + k_p C^* M \quad .\ .\ (4)$$

where $M$ = monomer concentration and $C^*$ = total concentration of radicals. For very long chains the growth reaction is much faster than that of initiation, and the first term will be negligible compared with the second.

In the steady state, $\frac{dC^*}{dt} = 0$, and the velocity of initiation equals the velocity of termination. This equality permits the calculation of $C^*$.

Since

$$V_{init} = V_{term}$$
$$= k_t C^{*2}.$$
$$C^* = \sqrt{\frac{V_{init}}{k_t}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and substituting in (4),

$$-\frac{dM}{dt} = V_{init} + k_p M \sqrt{\frac{V_{init}}{k_t}} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Equation (6) may be rearranged in a more useful form by introducing the kinetic chain length $\gamma$, which is defined as the number of monomers consumed per unit initiation process. Now $\gamma = V_{prop}/V_{init}$ and from equation (4) it follows that

$$-\frac{dM}{dt} = V_{prop}\left[1 + \frac{1}{\gamma}\right] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$
$$= k_p C^* M\left[1 + \frac{1}{\gamma}\right]$$
$$= k_p \left(\frac{V_{init}}{k_t}\right)^{\frac{1}{2}} M\left[1 + \frac{1}{\gamma}\right] \quad . \quad . \quad . \quad . \quad . \quad (8)$$

For long chains $\frac{1}{\gamma}$ is small and the term in the square brackets is approximately equal to unity and may be omitted from subsequent considerations. The overall rate of polymer formation may be derived by introducing the appropriate value for $V_{init}$. The following possibilities may be considered :

*a* Second order initiation

$$V_{init} = k_i M^2$$
$$-\frac{dM}{dt} = \frac{k_i^{\frac{1}{2}} k_p}{k_t^{\frac{1}{2}}} . M^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

which accounts for the second order dependence on monomer concentration for the polymerization of styrene in bulk and in solution.

*b* First order initiation

$$V_{init} = k_i M$$
$$-\frac{dM}{dt} = \frac{k_i^{\frac{1}{2}} . k_p}{k_t^{\frac{1}{2}}} . M^{3/2} \quad . \quad . \quad . \quad . \quad . \quad (10)$$

*c* Photochemical initiation

$$V_{init} = f(I)M$$

where $I$ = intensity of absorbed light.

$$-\frac{dM}{dt} = \left(\frac{f(I)}{k_t}\right)^{\frac{1}{2}} . k_p M^{3/2} \quad . \quad . \quad . \quad . \qquad (11)$$

*d* Catalysed initiation, in which the most general case would be a bimolecular reaction between the catalyst (which may be a simple free radical) and the monomer

$$V_{init} = k_i M B$$

whence
$$-\frac{dM}{dt} = \frac{k_i^{\frac{1}{2}} . k_p}{k_t^{\frac{1}{2}}} . M^{3/2} B^{\frac{1}{2}} \quad . \quad . \quad . \quad . \qquad (12)$$

a law observed in several benzoyl-peroxide-catalysed polymerizations.

An initiation velocity dependent on the concentration of catalyst and independent of monomer concentration would give a monomolecular overall rate

$$-\frac{dM}{dt} = \frac{k_i^{\frac{1}{2}} k_p}{k_t^{\frac{1}{2}}} . M B^{\frac{1}{2}} \quad . \quad . \quad . \quad . \qquad (13)$$

as observed by Price (*loc. cit.*) for *d*-*s*.-butyl-α-chloracrylate.

## DEGREE OF POLYMERIZATION AND KINETIC CHAIN LENGTH

For the above reaction scheme the kinetic chain length $\gamma$ is equal to the degree of polymerization, $\overline{DP}$, which is the number of repeating units in the polymer chain. A number of relationships may be derived for use as additional checks on the mechanism.

Since
$$\gamma = -\frac{dM}{dt} \Big/ V_{init} \quad . \quad . \quad . \quad . \quad . \qquad (14)$$

for a second order catalysed initiation reaction, $M + B \longrightarrow M_1{}^*$

$$\gamma = \frac{k_p}{(k_i k_t)^{\frac{1}{2}}} \cdot \frac{M^{\frac{1}{2}}}{B^{\frac{1}{2}}} \quad . \quad . \quad . \quad . \quad . \qquad (15)$$

and the degree of polymerization is proportional to the square root of the monomer concentration. In the case of the uncatalysed second order initiation

$$\gamma = \frac{k_p}{(k_i k_t)^{\frac{1}{2}}} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (16)$$

and the degree of polymerization is independent of the monomer concentration. The published data on the polymerization of styrene in solution in the presence and absence of benzoyl peroxide do not obey either of these relationships, and the results indicate that some other reaction is occurring which terminates polymer growth without terminating the chain reaction.

## CHAIN TRANSFER REACTIONS

The termination of growth without stopping the chain, as shown by MAYO [38] and EYRING [39], is due to a chain transfer reaction with either the monomer or the solvent, and it is therefore necessary to introduce transfer reactions into the above scheme.

*Transfer Reactions*

$$M_n^* + M \longrightarrow M_n + M_1^* \quad \textit{Monomer transfer.} \quad k_{tr} \quad . \quad (17)$$

$$\left.\begin{array}{l} M_n^* + S \longrightarrow M_n + S^* \\ S^* + M \longrightarrow M_1^* + S \end{array}\right\} \textit{Solvent transfer.} \quad \begin{array}{ll} k_{tr'} \; . & (18) \\ k_s \; . & (19) \end{array}$$

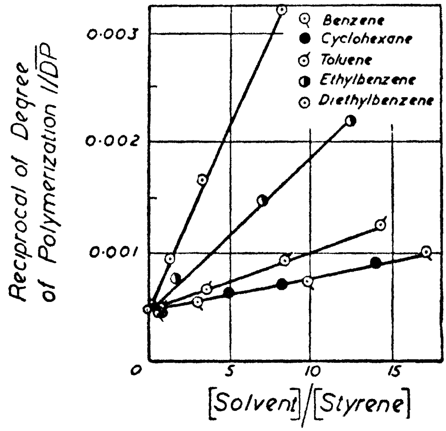


*Figure 10. Effect of solvents on the degree of polymerization of styrene at* 100°*C* (*Reference :* 38)

The degree of polymerization for small amounts of reaction is now given by

$$\overline{DP} = \frac{\textit{rate of chain growth}}{\textit{rate of chain termination by all processes}},$$

$$= \frac{k_p M C^*}{k_t C^{*2} + k_{tr} M C^* + k_{tr'} C^* S} \quad . \quad . \quad . \quad . \quad . \quad (20)$$

where $S$ denotes the concentration of solvent. Since as before for the catalysed reaction

$$C^* = \left(\frac{V_{init}}{k_t}\right)^{\frac{1}{2}} = \left[\frac{k_i M B}{k_t}\right]^{\frac{1}{2}}$$

it follows, by inverting equation (20) and substituting for $C^*$, that

$$\frac{1}{\overline{DP}} = \frac{(k_i k_t)^{\frac{1}{2}} B^{\frac{1}{2}}}{k_p M^{\frac{1}{2}}} + \frac{k_{tr}}{k_p} + \frac{k_{tr'}}{k_p} \cdot \frac{S}{M} \quad . \quad . \quad . \quad (21)$$

For the uncatalysed reaction, the first term of the above expression reduces to $(k_i k_t)^{\frac{1}{2}}/k_p$. In the absence of a solvent, the last term is zero and the average degree of polymerization in the pure monomer $\overline{DP}_0$ is given by

$$\frac{1}{\overline{DP}_0} = \frac{(k_i k_t)^{\frac{1}{2}}}{k_p} + \frac{k_{tr}}{k_p} \quad . \; . \; . \; . \; . \; . \quad (22)$$

In the general case of the uncatalysed reaction, equations (21) and (22) lead to

$$\frac{1}{\overline{DP}} = \frac{1}{\overline{DP}_0} + \frac{k_{tr'}}{k_p} \cdot \frac{S}{M}$$

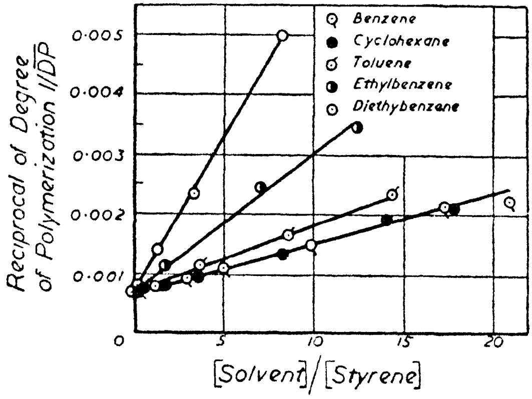


*Figure 11. Effect of solvents on the degree of polymerization of styrene at* 132°*C* (*Reference :* 38)

This equation may be tested by plotting $\frac{1}{\overline{DP}}$ against $\frac{S}{M}$, and should give a straight line with intercept $\frac{1}{\overline{DP}_0}$ and slope $k_{tr'}/k_p$. *Figures 10* and *11* show that this equation is obeyed by the polymerization of styrene in a number of solvents.

## RATES OF ELEMENTARY REACTIONS

Each of the basic processes of initiation, propagation and termination is characterized by a definite reaction velocity constant, and kinetically it is most important that we should have an unambiguous knowledge of the rates and activation energies of each of these elementary processes. It should then be possible to answer the more general questions of the relationship between molecular structure and chain growth, or the dependence of the propagation and termination reactions upon molecular size.

The real difficulty in evaluating these rate constants is that the usual measurements of *a* the total amount of polymer formed as a function of time under different conditions and *b* the determination of the kinetic chain length $\gamma$ or the number or weight average degree of polymerization, provide only two equations connecting the velocity constants of initiation $k_i$, propagation $k_p$, and termination, $k_t$. Hence these measurements alone are not sufficient for the unambiguous evaluation of the three constants. This may be seen more clearly from the expressions for $dM/dt$ and $\gamma$ derived in the previous section for the catalysed polymerization of styrene or methyl methacrylate, namely

$$-\frac{dM}{dt} = \frac{k_i^{\frac{1}{2}} k_p}{k_t^{\frac{1}{2}}} \, . \, M^{3/2} B^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad (23)$$

$$\gamma = \frac{k_p}{(k_i k_t)^{\frac{1}{2}}} \cdot \frac{M^{\frac{1}{2}}}{B^{\frac{1}{2}}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

By division of these equations we obtain

$$-\frac{1}{\gamma} \cdot \frac{dM}{dt} = k_i \, . \, MB = V_{init} \quad . \quad . \quad . \quad . \quad (25)$$

Thus the measurement of $-dM/dt$ and $\gamma$ may be used to determine the initiation velocity and hence $k_i$. Alternatively, the two equations may be used to derive the ratio, $k_p/k_t^{\frac{1}{2}}$, but cannot give either of these constants separately. The radical catalysed polymerization of styrene has been measured by many independent investigators, and it is agreed that the overall activation energy in the initial stages is about 23,000–25,000 cal/mol.[10, 39] Expressing the results in the kinetic form, $k_0 = Ae^{-E/RT}$, the value of $A$ is about $10^{11}$, and since, according to the experimental law (page 66), $-dM/dt = k_0 M^{3/2} B^{\frac{1}{2}}$, the velocity constant $k_0$ may be expressed

$$k_0 = k_i^{\frac{1}{2}} k_p / k_t^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

The initiation velocity determined from equation (25) leads to values of $A = 10^{12}$, $E = 29{,}000$ cal/mol.[39] This result is in good agreement with the value of $E = 28{,}000$ cal/mol determined from the rate of disappearance of benzoquinone inhibitor.[16] For the uncatalysed polymerization of styrene the activation energy is 23,000–28,000 cal/mol and the collision number is between $10^4$ and $10^6$.[39]

A knowledge of $k_0$ and the velocity constant of initiation $k_i$ permits, by use of equation (26), the evaluation of the ratio $k_p/k_t^{\frac{1}{2}}$, and hence the value of $E_p - \frac{1}{2}E_t$, where $E_p$ and $E_t$ are the activation energies of the propagation and termination reactions respectively. Published data on styrene correspond to values of $E_p - \frac{1}{2}E_t$ of 4,500–9,000 cal/mol. A similar order of magnitude for this difference has been observed with other monomers, and without other information all that may be concluded is that the activation energy of propagation must exceed the value of $E_p - \frac{1}{2}E_t$. Unfortunately, the kinetic relationships of the uncatalysed or peroxide catalysed reactions give no decision as to whether the termination reaction is by disproportionation or combination.

In order to determine the individual constants, $k_p$ or $k_t$, it is necessary to have a third independent expression containing measurable quantities. MELVILLE[40] has shown that one of these is the measurement of the lifetime of the active polymer molecule, P. In the stationary state we have

$$\textit{rate of production of } \mathrm{P} = \textit{rate of removal of } \mathrm{P} = \frac{[\mathrm{P}]}{\tau} \quad . \quad (27)$$

where [P] is the stationary concentration of P, and $\tau$ is its mean lifetime. The rate of production of active polymers may be determined *a* by the use of inhibitors as previously discussed, *b* from a knowledge of the rate of radical induced polymerizations, and *c* from the number of quanta absorbed in photochemical polymerizations, if it is known that each absorbed quantum starts a chain. The determination of $\tau$ was achieved by Melville by the use of photochemical excitation. The principle of the method can be seen readily in the following manner. A slotted disc is rotated at known speed in the light beam and the sectors are so constructed as to give equal periods of illumination and darkness. If $I$ is the intensity of light used with the sector, then, since there are equal periods of illumination and darkness, $\frac{I}{2}$ is the effective intensity, provided the period of illumination is short compared with the active life of the polymer molecule. If the rate of polymerization obeys equation (11) and is accurately proportional to the square root of the light intensity, the rate under the above conditions will be proportional to $\sqrt{\frac{I}{2}}$. If the disc is now rotated so slowly that the activated molecule is destroyed before the next period of illumination, then effectively the system will receive light of intensity $I$, but for half the period of the experiment, and hence the rate will now be proportional to $I^{\frac{1}{2}}/2$. The rate will thus be $\sqrt{2}$ times faster at higher rates of rotation of the sector. A mathematical analysis of the rate/frequency of flashing curve enables one to compute accurately the mean life of the active polymer. Since $\tau$ and $d[\mathrm{P}]/dt$ are known, [P] may be computed from (27). In the case of vinyl acetate, MELVILLE[41] showed that $[\mathrm{P}] = 1{\cdot}7 \times 10^{-8}$ mols/litre, or $10^{-9}$ of the concentration of the vinyl acetate molecules. Now, since

$$-\frac{dM}{dt} = k_p[\mathrm{P}]M,$$

$k_p$ may be determined. The results obtained by BURNETT and MELVILLE[41] and independently by BARTLETT and SWAIN[42] for the polymerization of vinyl acetate are summarized in *Table X.*

*Table X*

*Constants for the Photopolymerization of Vinyl Acetate*

| | *Burnett and Melville* | *Bartlett and Swain* |
|---|---|---|
| *Temperature, °C* | 15·9 | 25 |
| *Exciting wavelength, Å* | >2500 | >2998 |
| $\tau$, *sec* | 0·0225 | 1·25 |
| $k_p$(*l mol*$^{-1}$ *sec*$^{-1}$) | $5{\cdot}86 \times 10^2$ | $1{\cdot}1 \times 10^3$ |
| $k_t$(*l mol*$^{-1}$ *sec*$^{-1}$) | $3{\cdot}04 \times 10^9$ | $8 \times 10^7$ |

The cause of the differences between these two sets of results is not yet clear. Melville also determined the variation of $k_p$ with polymer chain length and was thus, for the first time, able to answer the very pertinent question—As the molecule grows, does the monomer find it more and more difficult to locate and add on to the end of the growing chain? The measurements in *Table XI* show that $k_p$ decreases only slightly on doubling the chain size.

*Table XI*

*Variation of $k_p$ with Chain Length for Vinyl Acetate*

| | | |
|---|---|---|
| *Chain length* | 174 | 339 |
| *Molecular weight* | 114,000 | 220,000 |
| $k_p$(*l mol*$^{-1}$ *sec*$^{-1}$) | $7{\cdot}7 \times 10^2$ | $6{\cdot}7 \times 10^2$ |

By carrying out measurements at a number of temperatures, the energy of activation for propagation was found to be 4,400 cal and the temperature independent factor for the propagation reaction, $A = 1{\cdot}5 \times 10^5$. Since the normal value of the temperature independent factor $A$ for a bimolecular reaction is about $10^{11}$ litre

$mol^{-1}sec^{-1}$, this implies a steric factor of $10^{-6}$, or that only one in every million collisions, in which the activation energy is present, leads to reaction.

The termination coefficient, $k_t$, can be computed from equation (26). The above data for $k_p$ together with the knowledge of $k_t$ determined by use of inhibitors (*loc. cit.*) lead to the following values for $k_t$.

*Table XII*

*Variation of $k_t$ with Chain Length for Vinyl Acetate*

| | | |
|---|---|---|
| *Chain length* . . . . | 174 | 339 |
| $k_t$ (*l mol*$^{-1}$ *sec*$^{-1}$) . . . | $3{\cdot}1 \times 10^9$ | $2{\cdot}5 \times 10^9$ |

These results show that $k_t$ is only slightly decreased with increase in molecular weight. Furthermore, experiment showed the value of $k_t$ to be unaffected by temperature, and hence no activation energy is necessary for reaction of the active polymers. The steric factor is only $10^{-2}$, and thus the active ends of the long chains have little difficulty in colliding and reacting. These results indicate that $k_p/k_t^{\frac{1}{2}}$ is little dependent on molecular size. (See *Appendix* at end of this Chapter for a further development in the determination of the individual velocity constants.)

## IV

## MOLECULAR WEIGHT DISTRIBUTION

A further expression combining the same velocity constants, $k_t$, $k_p$, and $k_t$, with directly measurable quantities is given by the distribution of molecular sizes of the polymer formed. On the basis of any proposed reaction scheme it is possible, at least in principle, to derive the theoretical distribution curve as a function of time, and of the various rate constants. Different types of initiation and termination mechanism lead to different forms of molecular weight distribution curves, and a comparison of the experimentally determined distribution with that calculated for a proposed mechanism can be used to check the kinetic relationships. Where the kinetics cannot be completely determined, the distribution curve may be used to provide additional data which may allow a decision between alternative mechanisms to be made. If the theoretical distribution expression, based on the rates of the individual reactions, is of simple form and can be justified experimentally, then it may provide a third equation which, in combination with the expressions for the rate of polymerization and kinetic chain length, enables the individual constants to be evaluated. Recently, the theoretical distribution of molecular size has been worked out for a number of kinetic mechanisms,[43] but only in a few instances has it been compared with experimental results. It is beyond the scope of this chapter to describe these elaborate calculations, and it will be sufficient if we work out a few cases as an illustration of the general method and summarize briefly the results of the more specialized calculations.

Consider the case of catalysed initiation, including both solvent and monomer transfer reactions and termination by disproportionation or combination. The general reactions for the catalysed polymerization may be represented by the scheme

| | | *Reaction velocity constant* |
|---|---|---|
| *Initiation* | $M + B \longrightarrow M_1^*$ | $k_i$ |
| *Propagation* | $M_1^* + M \longrightarrow M_2^*$ | $k_p$ |
| | $M_2^* + M \longrightarrow M_3^*$ | $k_p$ |
| | $M_r^* + M \longrightarrow M_{r+1}^*$, *etc* | $k_p$ |
| *Monomer transfer* | $M_r^* + M \longrightarrow M_r + M_1^*$ | $k_x$ |
| *Solvent transfer* | $M_r^* + S \longrightarrow M_r + S^*$ | $k_{x'}$ |
| | $S^* + M \longrightarrow M_1^* + S$ | $k_s$ |
| *Termination by disproportionation* | $M_r^* + M_s^* \longrightarrow M_r + M_s$ | $k_d$ |
| *Termination by recombination* | $M_r^* + M_s^* \longrightarrow M_{r+s}$ | $k_c$ |

In order to calculate the molecular weight distribution, it is necessary to derive equations for $dM_r/dt$. From the above set of reactions we obtain

$$\frac{dM_r}{dt} = k_x M_r^* M + k_{x'} M_r^* S + k_d M_r^* C^* + \tfrac{1}{2} k_c \sum_{j=1}^{j=r-1} M_j^* M^*_{r-j} \quad (28)$$

where $C^*$ = total concentration of radicals $= \sum_{r=1}^{r=\infty} M_r^*$ . . (29)

and

$$-\frac{dM}{dt} = k_i \,.\, MB + k_p C^* M + k_x C^* M + k_s S^* M - k_x M_1^* M - k_{x'} M_1^* S - k_d M_1^* C^* \quad (30)$$

Assuming that in the stationary states $\frac{dM_1^*}{dt}$, $\frac{dM_r^*}{dt}$ and $\frac{dS^*}{dt}$ are each equal to zero

$$\frac{dM_1^*}{dt} = k_i \,.\, MB - k_p M_1^* M + k_x M C^* - k_x M M_1^* - k_{x'} M_1^* S + k_s S^* M - k_d M_1^* C^* - k_c M_1^* C^* = 0 \quad (31)$$

$$\frac{dM_r^*}{dt} = k_pMM^*_{r-1} - k_pM_r^*M - k_xM_r^*M - k_{x'}M_r^*S - k_dM_r^*C^* - k_cM_r^*C^* = 0 \tag{32}$$

$$\frac{dS^*}{dt} = k_{x'}SC^* - k_sS^*M = 0 \tag{33}$$

Solving these equations for $M_1^*$, $M_r^*$, and $S^*$, it follows that

$$M_1^* = \frac{k_iMB + k_xMC^* + k_sS^*M}{k_pM + k_xM + k_{x'}S + k_dC^* + k_cC^*} \tag{34}$$

$$\frac{M_r^*}{M_{r-1}^*} = \frac{k_pM}{k_pM + k_xM + k_{x'}S + k_dC^* + k_cC^*} = q \tag{35}$$

and

$$\begin{aligned} C^* &= M_1^* + M_2^* + M_3^* + \ldots \\ &= M_1^* + qM_1^* + q^2M_1^* \ldots = M_1^* \sum_{q=0}^{q=\infty} q^n = \frac{M_1^*}{1-q} \end{aligned} \tag{36}$$

and hence from equations (34) and (35)

$$C^* = \left(\frac{k_i \,.\, MB}{k_d + k_c}\right)^{\frac{1}{2}} \tag{37}$$

a result previously derived (page 70) by simpler methods.

Rearranging equation (30)

$$\begin{aligned} -\frac{dM}{dt} &= (k_p + k_x)MC^*\left[1 + \frac{k_i \,.\, B}{(k_p + k_x)C^*} + \frac{k_sS^*}{(k_p + k_x)C^*} \right. \\ &\qquad \left. - \frac{k_xM_1^*}{(k_p + k_x)C^*} - \frac{k_{x'}SM_1^*}{(k_p + k_x)MC^*} - \frac{k_dM_1^*}{(k_p + k_x)M}\right] \\ &= (k_p + k_x)MC^*\left[1 + \frac{(k_d + k_c)C^*}{(k_p + k_x)M} + \frac{k_sS^*}{(k_p + k_x)C^*} \right. \\ &\qquad \left. - \frac{k_xM_1^*}{(k_p + k_x)C^*} - \frac{k_{x'}SM_1^*}{(k_p + k_x)MC^*} - \frac{k_dM^*}{(k_p + k_x)M}\right] \end{aligned}$$

$\approx (k_p + k_x)MC^*$ for long chains, since all other terms in the expression are very small compared to unity.

Therefore

$$\frac{\dfrac{dM_r}{dt}}{-\dfrac{dM}{dt}} = -\frac{dM_r}{dM}$$

$$= \frac{k_dM_r^*C^* + k_xM_r^*M + k_{x'}M_r^*S + \frac{1}{2}k_c \sum_{j=1}^{j=r-1} M_j^*M_{r-j}}{(k_p + k_x)MC^*}$$

From equation (35), $M_r{}^* = M_1{}^* q^{r-1}$, and by summation

$$-\frac{dM_r}{dM} = \frac{k_d}{k_p + k_x} \cdot \frac{M_1{}^*}{M} \cdot q^{r-1} + \frac{(k_x M + k_{x'} S) M_1{}^* q^{r-1}}{(k_p + k_x) MC^*} + \frac{\frac{1}{2} \cdot k_c M_1{}^{*2} (r-1) q^{r-2}}{(k_p + k_x) MC^*} \quad . \quad (38)$$

This is a general equation which embraces all special cases. In view of its unwieldy nature, its application may be best considered for two simple cases.

*Case 1*—Uncatalysed bimolecular initiation reaction; that is, $M = B$, in which all transfer reactions are ignored and termination is entirely by disproportionation.

Setting $k_x = k_{x'} = k_s = k_c = 0$ in equation (38)

$$-\frac{dM_r}{dM} = \frac{k_d}{k_p} \cdot \frac{M_1{}^*}{M} \cdot q^{r-1} \quad . \quad . \quad . \quad . \quad . \quad (39)$$

Since from (35) and (37)

$$q = \frac{k_p M}{k_p M + k_d C^*} = \frac{k_p}{k_p + k_d{}^{\frac{1}{2}} k_i{}^{\frac{1}{2}}} = \frac{1}{1 + \varepsilon}$$

where $$1/\varepsilon = \frac{k_p}{k_i{}^{\frac{1}{2}} \cdot k_d{}^{\frac{1}{2}}}$$

and from previous considerations $\varepsilon = 1/\gamma$, where $\gamma$ = kinetic chain length.

From (34) and (37),

$$M_1{}^* = \frac{k_i M^2}{k_p M + k_d C^*} = \frac{k_i M}{k_p + k_i{}^{\frac{1}{2}} k_d{}^{\frac{1}{2}}}$$

and it follows, on substituting for $q$ and $M_1{}^*$ in (39)

that $$-\frac{dM_r}{dM} = \frac{k_d k_i}{k_p{}^2} \cdot \frac{k_p}{k_p + (k_d k_i)^{\frac{1}{2}}} \left(\frac{1}{1+\varepsilon}\right)^{r-1}$$

$$= \varepsilon^2 \left(\frac{1}{1+\varepsilon}\right)^r \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (40)$$

Integrating (40), $$M_r = \varepsilon^2 \left(\frac{1}{1+\varepsilon}\right)^r (M_0 - M) \quad . \quad . \quad . \quad . \quad (41)$$

where $M_0$ is the initial concentration of monomer and $(M_0 - M)$ is the total weight of polymer at any monomer concentration, $M$.

The weight fraction $w_r$ of the $r$th polymer is consequently given by

$$w_r = \frac{rM_r}{(M_0 - M)}$$

$$= r\varepsilon^2 \left(\frac{1}{1 + \varepsilon}\right)^r \quad . \quad . \quad . \quad . \quad . \quad . \quad (42)$$

The number and weight average chain lengths $\nu_n$ and $\nu_w$ respectively may be computed as follows

$$\nu_n = \frac{\sum\limits_{r=2}^{r=\infty} rM_r}{\sum\limits_{r=2}^{r=\infty} M_r}$$

The sum in the numerator is $(M_0 - M)$ and

$$\sum_{r=2}^{r=\infty} M_r = \sum_{r=2}^{r=\infty} \varepsilon^2 \left(\frac{1}{1+\varepsilon}\right)^r (M_0 - M)$$

$$= \sum_{r=2}^{r=\infty} \varepsilon^2 \left(\frac{1}{1+\varepsilon}\right)\left(\frac{1}{1+\varepsilon}\right)^{r-1} (M_0 - M)$$

$$= \varepsilon^2 \left(\frac{1}{1+\varepsilon}\right)\left\{\frac{1}{(1+\varepsilon)} + \frac{1}{(1+\varepsilon)^2} + \frac{1}{(1+\varepsilon)^3} \cdots\right\}(M_0 - M)$$

and when $\varepsilon$ is small ($r$ is large), the series converges rapidly to $1 + \frac{1}{\varepsilon}$. Thus

$$\sum_{r=2}^{r=\infty} M_r = \varepsilon^2 \cdot \frac{1}{(1+\varepsilon)} \cdot \left(1 + \frac{1}{\varepsilon}\right)(M_0 - M) = \varepsilon(M_0 - M)$$

and therefore

$$\nu_n = \frac{(M_0 - M)}{\varepsilon(M_0 - M)} = \frac{1}{\varepsilon} = k_p/k_i^{\frac{1}{2}}k_d^{\frac{1}{2}} \quad . \quad . \quad . \quad (43)$$

which is equivalent to the previously derived equation (page 70). The weight average chain length

$$\nu_w = \frac{\sum\limits_{r=2}^{r=\infty} r^2 M_r}{\sum\limits_{r=2}^{r=\infty} rM_r}$$

may likewise be computed by series summation, and is given by

$$\nu_w = \frac{2}{\varepsilon} = 2 \cdot \frac{k_p}{k_i^{\frac{1}{2}}k_d^{\frac{1}{2}}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (44)$$

It will be noted that, for this particular mechanism, the weight average is twice that of the number average chain length. Both values are independent of the initial monomer concentration and of the extent of the reaction.

*Case 2*—Uncatalysed bimolecular initiation with the pure monomer and termination by recombination; that is, $S = 0$, $k_{x'} = k_s = k_x = k_d = 0$.

Equation (38) then reduces to

$$-\frac{dM_r}{dM} = \tfrac{1}{2}\frac{k_c M_1{}^{*2}(r-1)q^{r-2}}{k_p M C^*} \quad . \quad . \quad . \quad (45)$$

As before, $q = \dfrac{1}{1+\varepsilon}$, $C^* = \left(\dfrac{k_i \, . \, M^2}{k_c}\right)^{\frac{1}{2}}$ and from (34)

$$M_1{}^* = \frac{k_i M}{k_p + k_i{}^{\frac{1}{2}} k_c{}^{\frac{1}{2}}}$$

Substituting in (45)

$$-\frac{dM_r}{dM} = \tfrac{1}{2}\left(\frac{k_i M}{k_p + k_c{}^{\frac{1}{2}} k_i{}^{\frac{1}{2}}}\right)^2 \cdot \frac{k_c{}^{3/2}}{k_p \, . \, k_i{}^{\frac{1}{2}} M^2}(r-1)\left(\frac{1}{1+\varepsilon}\right)^{r-2}$$

$$= \tfrac{1}{2}\varepsilon^3(r-1)\left(\frac{1}{1+\varepsilon}\right)^r \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (46)$$

Therefore

$$M_r = \int_M^{M_0} \frac{r-1}{2} \cdot \frac{\varepsilon^3}{(1+\varepsilon)^r} \, . \, dM$$

$$= \frac{r-1}{2} \cdot \frac{\varepsilon^3}{(1+\varepsilon)^r}(M_0 - M) \quad . \quad . \quad . \quad (47)$$

Adopting the methods employed above, the weight and number average chain lengths may be found by summing the appropriate series, and are given by

$$\nu_w = \frac{3}{\varepsilon} \text{ and } \nu_n = \frac{2}{\varepsilon}$$

That is, the mean chain length is independent of the concentration of the monomer, and that for this mechanism $\nu_w/\nu_n = 3/2$.

In order to illustrate the principles of the method of calculation of the molecular weight distribution, we have selected two rather simple cases in which the initiation was second order with respect to the monomer concentration and termination was either by disproportionation or recombination of two active polymers. Initiation may also occur by a zero or first order process with respect to the monomer concentration. Types of termination other than mutual destruction of active chains have been postulated—namely, *a* monomer deactivation; that is, destruction of the activity of the growing polymer by a particular type of collision with a monomer molecule; *b* spontaneous termination in which the active polymer reverts to a stable form. On the basis of any of these reaction schemes, the distribution of molecular weights may be worked out theoretically by a procedure identical with the foregoing. In carrying through these calculations two assumptions have been made: (i) that all the active polymers are identical in reactivity; that is, the velocity constant of propagation $k_p$ is independent of molecular size; (ii) that the stationary state method is applicable. The latter condition applies to those reactions in which the mean life of the active centres is very small compared with the half life of the reaction. The polymerization of styrene, vinyl acetate, and other vinyl compounds satisfies this requirement. The theoretical types of distribution curve for various reaction schemes based on the above assumptions have been extensively examined by GEE and MELVILLE.[43] Some of the results of these authors are brought together in *Table XIII*.

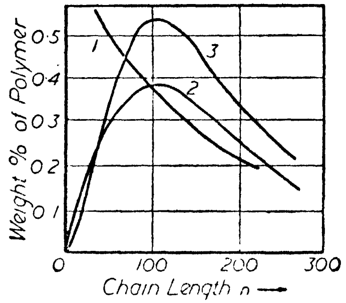


*Figure 12. Molecular weight distribution curves for various types of polymerization reaction*

*Curve 1. Photoinitiation, mutual destruction by combination*
$k_p^{\frac{1}{2}}/k_c f(I)^{\frac{1}{2}} = 10^{-2}$

*Curve 2. 2nd order initiation, mutual destruction by disproportionation*
$k_i^{\frac{1}{2}} k_p^{\frac{1}{2}}/k_d = 10^{-2}$

*Curve 3. 2nd order initiation, mutual destruction by combination*
$k_i^{\frac{1}{2}} k_p^{\frac{1}{2}}/k_c = 2 \times 10^{-2}$

(*Reference* : 43)

The first column shows the quantities which can be measured in a polymerization process, and from an examination of the data it will be seen at once how the various modes of initiation and termination affect the molecular distributions. In order to make the distinction clearer, some of the distribution curves are plotted in *Figure 12*.

A comparison of the experimental distribution with that of theory for any kinetic mechanism may, therefore, be used as an additional check on the kinetics. ROBERTSON and HERINGTON[44] have discussed the use of distribution curves for the study of the mechanism of polymerization reactions, but up to the present time the method has been employed in only a few cases. This defect is due mainly to the difficulties of the present laborious methods of fractionation, and extensive application of these methods must await the develop-

## *Table XIII*
## *Velocity, Chain Length, and Distribution Functions*

| *Termination mechanism* | *Initiation* | | |
|---|---|---|---|
| | *Photochemical* | *First order* | *Second order* |
| *Monomer* | | | |
| $-dM/dt$ | $f(I) . k_p/k_t$ | $k_i k_p/k_t . M$ | $k_i k_p/k_t . M^2$ |
| $\bar{\nu}_n = \frac{1}{2}\bar{\nu}_w$ | $k_p/k_t$ | $k_p/k_t$ | $k_p/k_t$ |
| $w_r$ *(end of reaction)* | $k_t/k_p . r(1 + k_t/k_p)^{-r}$ *for all initiating mechanisms* | | |
| *Mutual disproportionation* | | | |
| $-dM/dt$ | $f(I)^{\frac{1}{2}} . k_p/k_d . M$ | $k_i^{\frac{1}{2}} k_p/k_d^{\frac{1}{2}} . M^{3/2}$ | $k_i^{\frac{1}{2}} k_p/k_d^{\frac{1}{2}} . M^2$ |
| $\bar{\nu}_n$ | $\dfrac{(M)_0 - M}{k_d^{\frac{1}{2}}/k_p . f(I)^{\frac{1}{2}} \ln\left\{\dfrac{(M)_0 + k_d^{\frac{1}{2}}/k_p . f(I)^{\frac{1}{2}}}{(M) + k_d^{\frac{1}{2}}/k_p . f(I)^{\frac{1}{2}}}\right\}}$ | $\dfrac{(M)_0^{\frac{1}{2}} + (M)^{\frac{1}{2}}}{2k_i^{\frac{1}{2}} . k_d^{\frac{1}{2}}/k_p}$ | $k_i^{-\frac{1}{2}} . \dfrac{k_p}{k_d^{\frac{1}{2}}}$ |
| $\bar{\nu}_w$ | $\dfrac{(M)_0 + M}{f(I)^{\frac{1}{2}} . k_d^{\frac{1}{2}}/k_p}$ | — | $2\dfrac{k_d^{\frac{1}{2}}}{k_p} . k_i^{-\frac{1}{2}}$ |
| $w_r$ | $\dfrac{k_d^{\frac{1}{2}}}{k_p} . f(I) \left\{1 + \dfrac{k_d^{\frac{1}{2}}}{k_p} . f(I)/(M)_0\right\}^{-r} (M)_0$ | — | $\dfrac{r\dfrac{k_d}{k_p^2} . k_i}{\left(1 + \dfrac{k_i k_d^{\frac{1}{2}}}{k_p}\right)^r}$ |

NOTE.—$k_t$ and $k_d$ represent the velocity constants for monomer and mutual disproportion termination reactions.

ment of a more rapid and accurate method for the determination of the distribution curves.

SCHULZ[45] has determined the distribution of molecular weights of polystyrene polymerized in solution without a catalyst, and equation (46) was found to fit the observed distribution curves approximately. His treatment was not, however, rigorous, since the value of $k_c^{\frac{1}{2}}/k_p$ was determined from the maximum in the observed distribution curve. In only one case has a direct comparison been made of the theoretical and experimental distribution curves for a reaction in which the kinetics of polymerization have been established in detail. This has been achieved by BAXENDALE, BYWATERS, and EVANS[46] for the hydroxyl radical catalysed polymerization of methyl methacrylate. Employing the reaction scheme given later (page 94), the theoretical distribution curves were calculated by the method of stationary states. The distribution relationship obtained was

$$\frac{dM_r}{dM} = \frac{a_0{}^3\beta^3(r - 2)}{2M_0{}^3}\left[\frac{M}{M_0}\right]^{3\beta}\left\{1 + \frac{a_0\beta}{M_0}\left(\frac{M}{M_0}\right)^{\beta}\right\}^{r}$$

where $M_r$ is concentration of polymer of chain length $r$, $\beta = \sqrt{k_1 k_t/k_p}$, $a_0$ = initiator concentration, and $M_0$ = initial monomer concentration. The weight distribution curve as a function of $M/M_0$ was obtained by a graphical integration of the above equation. *Figure 13* shows a comparison of the theoretical distribution curve with the experimental curves obtained by a single and a double fractionation.

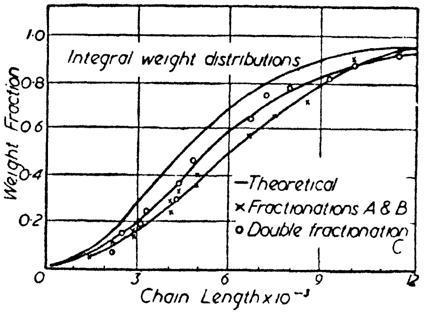


*Figure 13. Comparison of theoretical and integral weight distributions for polymethyl methacrylate*

(*Reference* : 46)

## CONSTRUCTION OF DISTRIBUTION CURVES

The theory of the separation of a heterogeneous polymer into a series of fractions, differing in average molecular weight, will be discussed in Chapter 4. The results of such a fractionation can be conveniently represented graphically by plotting the total weight of all molecules removed from the original sample, or, alternatively, the weight of each of the fractions, against the average molecular weight of the fraction, determined by one of the methods described later. In this way a steplike graph is obtained. Since it is justifiable to regard the polymolecularity as a continuous and not a discontinuous function, the stepwise curve may be replaced by a continuous line. The accuracy of this representation depends, of course, on the number and the width of the fractions. The narrower the interval, the better is the result of the construction of the continuous curve. Unless the fractions are very sharp, the actual width of each polymer band is somewhat a matter of guesswork, and it must be remembered that fractions will contain polymers of chain length above and below the measured chain length of the fraction. To obtain the distribution curve it is assumed *a* that the distribution of chain lengths in each fraction is symmetrical about the measured chain length, and *b* that in constructing the integral weight curve only the fraction to which the weight is summed contains polymers of chain length above that of the mean. Thus, to obtain a point ($w_r - r$) on the curve, the weight fractions up to and including the fraction of measured chain length $r$ are summed, and assuming *a* and *b*, one half of the weight of the last fraction is subtracted. The values of the integral weight $w_r$ obtained in this way by BAXENDALE, BYWATERS, and EVANS [46] for the fractionation of methyl

*Table XIV*

*Typical Fractionation of a Polymer*

*Methyl methacrylate formed with* $Fe^{++}$ *and* $H_2O_2$ *as initiator and precipitated from acetone with aqueous acetone* [46]

| *Fraction* | *Actual weight in g* | *Chain length* | *Weight fraction up to r* ($w_r$) |
|---|---|---|---|
| 1 | 0·220 | 10,500 | 0·978 |
| 2 | 1·259 | 9,750 | 0·904 |
| 3 | 1·177 | 8,390 | 0·783 |
| 4 | 0·963 | 7,310 | 0·674 |
| 5 | 0·671 | 6,470 | 0·592 |
| 6 | 0·765 | — | — |
| 7 | 0·580 | — | — |
| 8 | 0·352 | 4,930 | 0·406 |
| 9 | 0·389 | 4,830 | 0·369 |
| 10 | 0·304 | 4,240 | 0·335 |
| 11 | 0·566 | 4,040 | 0·290 |
| 12 | 0·278 | 4,070 | 0·248 |
| 13 | 0·534 | 3,430 | 0·207 |
| 14 | 0·416 | 2,940 | 0·160 |
| 15 | 0·512 | 2,140 | 0·112 |
| 16 | 0·328 | 1,710 | 0·070 |
| 17 | 0·154 | 1,269 | 0·046 |

methacrylate are shown in Table XIV. In the last column the weight $w_r$ is expressed as a fraction of the total amount of polymer up to chain length $r$. Usually one is more interested in the weight of molecules belonging to a narrow range, such as that between $r$ and $r + dr$. This information is obtained from the differential weight distribution curve which is derived by graphical differentiation of the integral weight distribution curve. It is obvious that any inflexion point on the integral curve corresponds to a maximum or minimum in the distribution curve, whilst a steep portion corresponds to a high concentration of molecules in that range. This is illustrated in *Figure 14*, which is the differential weight distribution derived from *Figure 13*.

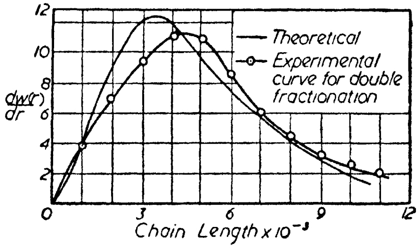


*Figure 14. Comparison of theoretical and experimental differential weight distributions for polymethyl methacrylate*
(*Reference* : 46)

The same data may obviously be used to obtain integral number and differential number distribution curves, since the weight of one chain of $r$ links is $rm_0$, where $m_0$ is the molecular weight of the fundamental unit.

## V

## COPOLYMERIZATION *

When the material undergoing polymerization consists of a mixture of two or more unsaturated monomers, the addition polymer formed is built up of units from each of the monomers. Such a polymer is known as a copolymer or interpolymer. It is an interesting fact that the individual monomers undergoing copolymerization may not polymerize alone. A copolymer formed with the latter type of monomer is often called a heteropolymer.

With the polymers obtained from a single monomeric unit no serious problems of chemical composition arise except in regard to the nature of the end groups. In the case of copolymers, however, the question of composition is of major importance. This is true not only because the ratio of monomers in the copolymer is variable, but also because polymer molecules prepared in the same batch have quite different compositions. When a mixture of two monomers undergoes polymerization, the polymer formed at any instant does not necessarily have the same composition as the mixture from which it is derived. The monomer ratio, however, determines the composition of the polymer; but, except in special cases, the composition changes throughout the polymerization. Accordingly, if one starts with a given monomer charge, the composition of the copolymer at the beginning of polymerization will be different from that at the end, and the resulting copolymer obtained when polymerization of the mixture is taken to completion will be very heterogeneous in composition. This general observation may be illustrated by the following simple kinetic considerations.[47] If two kinds of monomer $M_1$ and $M_2$ disappear by first order reactions, then

---

* The symbols used in this section are those recently recommended by Alfrey, Mayo and Wall, *J. Polymer Sci.* 1 (1946) 581. The ratios $r_1$ and $r_2$ correspond to $1/\alpha$ and $\beta$ of Alfrey and Goldfinger,[49] to $\sigma$ and $\mu$ of Mayo and Lewis [50] and to $\sigma$ and $\rho$ of Wall.[47]

$$\frac{dM_1}{dt} = -k_1 M_1$$

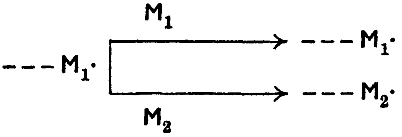
$$\frac{dM_2}{dt} = -k_2 M_2$$

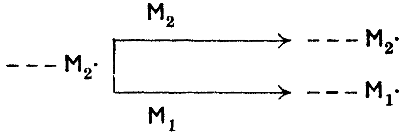
and by division

$$\frac{dM_1}{dM_2} = \frac{k_1 M_1}{k_2 M_2} = \alpha \frac{M_1}{M_2}$$

where $\alpha$ is the ratio of the two velocity constants. If $\alpha$ is not unity, the composition of the polymer at any instant will not be the same as that of the reacting mixture.

The above simple theory does not represent the behaviour of many systems, since, as first pointed out by NORRISH and BROOKMAN,[48] the rate of polymerization of a pair of monomers, based on a free radical mechanism, is governed by four chain growth processes determined by the reaction of the two kinds of radicals with $M_1$ and $M_2$. Two types of growing chains are possible, ending respectively in $M_1\cdot$ and $M_2\cdot$ type radicals, according as the active centre at the instant chosen ends in an $M_1$ or an $M_2$ unit, and these may react with either type of monomer.





*Relative Rates of Polymerization*—In the catalysed polymerization of a pair of monomers $M_1$ and $M_2$, the rate of formation of active nuclei $M_1{}^*$ and $M_2{}^*$ may be a bimolecular process given by

$$\frac{dM_1{}^*}{dt} = k^{m_1} . CM_1 . \quad . \quad . \quad . \quad . \quad (48)$$

$$\frac{dM_2{}^*}{dt} = k^{m_2} . CM_2 . \quad . \quad . \quad . \quad . \quad (49)$$

where $C$ is the concentration of the catalyst and the superscripts $m_1$ or $m_2$ refer to the nature of the monomer involved in the initiation process. Other types of initiation process, such as photoactivation, are, of course, possible. As explained above, four propagation processes occur, and these may be represented in terms of polymer endings in the following manner :

$$M_1{}^* + M_1 \xrightarrow{k_{11}} M_1{}^*.$$

$$M_1{}^* + M_2 \xrightarrow{k_{12}} M_2{}^*$$

$$M_2{}^* + M_2 \xrightarrow{k_{22}} M_2{}^*$$

$$M_2{}^* + M_1 \xrightarrow{k_{21}} M_1{}^*$$

Then for the rate of disappearance of the monomer $M_1$, neglecting any loss in the initiation process, we have

$$-\frac{dM_1}{dt} = k_{11}M_1{}^*M_1 + k_{21}M_1M_2{}^* \quad . \quad . \quad (50)$$

and for monomer $M_2$

$$-\frac{dM_2}{dt} = k_1M_1{}^*M_2 + k_{22}M_2{}^*M_2 \quad . \quad . \quad . \quad (51)$$

Finally, the chain termination reaction, as with simple polymerization, may involve mutual destruction by combination or disproportionation of any of the radical chains ending in $M_1{}^*$ and $M_2{}^*$. Chain transfer reactions may also have to be considered. The complete kinetic analysis of a copolymerization reaction is obviously very complex, and will involve at least two initiation, four propagation, and two termination reactions. By the assumption of steady state conditions, the stationary concentrations of $M_1^*$ and $M_2^*$ can be worked out as in the case of a single monomer, and a relationship determined for the overall rate of consumption of monomers $M_1$ and $M_2$ and for the average degree of polymerization. This expression, whilst mathematically straightforward, is algebraically complicated and contains too many constants to be subjected to experimental check, except in special cases. A simplified solution of the equation[49], which can be tested experimentally, can be obtained if it is assumed that the contribution of the initiation and termination reactions to the composition of the polymer is negligible. This is a good approximation if the molecular weight is high. By considering the four propagation processes only, the correct composition and distribution in the interior of the chains may be determined. In the steady state the rate of formation of $M_1^*$ is equal to the rate of consumption of $M_1^*$

$$k_{21}M_2{}^*M_1 = k_{12}M_1{}^*M_2$$

The same equation determines the stationary condition for $M_2^*$ and, stated in an alternative form, it means that in the steady state the reaction rate of polymers ending in $M_1^*$ with the monomer $M_2$ must equal the reaction rate of polymers ending in $M_2^*$ with monomer $M_1$.

It follows that

$$M_2{}^* = \frac{k_{12}}{k_{21}}\cdot\frac{M_2}{M_1}\cdot M_1{}^* \quad . \quad . \quad . \quad . \quad . \quad (52)$$

Therefore on substituting for $M_2^*$ in equations (50) and (51)

$$-\frac{dM_1}{dt} = M_1{}^*(k_{11}M_1 + k_{12}M_2)$$

and

$$-\frac{dM_2}{dt} = M_1{}^*\left(k_{12}M_2 + \frac{k_{22}\,.\,k_{12}}{k_{21}}\cdot\frac{M_2{}^2}{M_1}\right)$$

which give for the ratio

$$\frac{dM_1}{dM_2} = \frac{M_1}{M_2}\cdot\frac{k_{21}}{k_{12}}\left(\frac{k_{11}M_1 + k_{12}M_2}{k_{21}M_1 + k_{22}M_2}\right) \quad . \quad . \quad (53)$$

Introducing the variables $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$

$$\frac{dM_1}{dM_2} = \frac{M_1}{M_2}\cdot\frac{r_1M_1 + M_2}{r_2M_2 + M_1} \quad . \quad . \quad . \quad . \quad (54)$$

This equation expresses the ratio of the rates of addition of the two monomers to the chain and also the ratio of the two monomers in the resulting polymer. It is strictly applicable to experimental data relating to low percentages of copolymerization when $M_1/M_2$ may be assumed to be constant. For higher conversion, the integrated form, which will be given later, should be used.

It is convenient to discuss special cases of copolymerization in terms of equation (54). In the case of equimolecular quantities of the starting materials—that is, $[\mathrm{M}_1]_0 = [\mathrm{M}_2]_0$—the ratio of the two monomers in the resulting polymer which may be denoted by $[\mathrm{M}_2]_p/[\mathrm{M}_1]_p$ is given by

$$[\mathrm{M}_2]_p/[\mathrm{M}_1]_p = \frac{1 + r_2}{1 + r_1} \quad . \quad . \quad . \quad . \quad (55)$$

It is seen that unless $r_2 = r_1$, the initial polymer does not possess the same composition as the monomer mixture. In general, this is only true when

$$\frac{r_2 M_2 + M_1}{r_1 M_1 + M_2} = 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (56)$$

and only in the further case when $r_2 = r_1 = 1$ is the initial polymer of the same composition as the starting material, regardless of the concentration of $\mathrm{M}_1$ and $\mathrm{M}_2$.

When equation (56) is not obeyed, the initial polymer is relatively richer in one or other of the components. The more reactive of the monomers is used up the more rapidly, and the initial polymer will be richer in this constituent. The mixture therefore becomes relatively poorer in this component during polymerization. It necessarily follows that the polymers formed in the later stages of the reaction are relatively richer in the less reactive component. The net result is that the polymer formed when the reaction is taken to completion is a heterogeneous mixture of copolymer molecules of different compositions and chain lengths. The integration of equation (54) gives a relationship between the amount of polymer formed and its composition. This integration, which is somewhat complex, has been performed by MAYO and LEWIS [50] with the result

$$\log \frac{[\mathrm{M}_2]}{[\mathrm{M}_2]_0} = \frac{r_2}{1 - r_2} \cdot \log \frac{[\mathrm{M}_2]_0}{[\mathrm{M}_1]_0} \cdot \frac{M_1}{M_2} - \frac{1 - r_1 r_2}{(1 - r_1)(1 - r_2)} \log \frac{(r_1 - 1)\dfrac{[\mathrm{M}_1]}{[\mathrm{M}_2]} - r_2 + 1}{(r_1 - 1)\dfrac{[\mathrm{M}_1]_0}{[\mathrm{M}_2]_0} - r_2 + 1}$$

where $[M_1]_0$ and $[M_2]_0$ are the initial concentrations of $M_1$ and $M_2$. The equation, on transformation, becomes

$$r_2 = \frac{\log \frac{[M_2]_0}{[M_2]} - \frac{1}{p}\log \frac{1 - p\frac{[M_1]}{[M_2]}}{1 - p\frac{[M_1]_0}{[M_2]_0}}}{\log \frac{[M_1]_0}{[M_1]} + \log \frac{1 - p\frac{[M_1]}{[M_2]}}{1 - p\frac{[M_1]_0}{[M_2]_0}}}$$

where $$p = \frac{1 - r_1}{1 - r_2}.$$

This equation may be solved graphically.

Technically, the more important problem is to prevent the variation of composition with the extent of polymerization. As pointed out by ALFREY and GOLDFINGER,[49] if $r_1$ and $r_2$ are known for a pair of monomers, it should be possible to prepare a copolymer of composition $[M_2]_p/[M_1]_p = x$ by starting with a monomer mixture in which the two components have the relative composition $[M_2]_0/[M_1]_0 = y$, where $y$ is determined (equation 54) by $x$, $r_1$, and $r_2$ according to

$$y = \frac{x - 1 + [(x - 1)^2 + 4r_1r_2 \,.\, x]^{\frac{1}{2}}}{2r_2}$$

The choice of the initial monomer concentration determined by this equation gives an initial polymer of the desired composition, but as copolymerization proceeds the polymer formed will become richer in the less reactive component. If it is desired to produce a uniform polymer, then not only must the starting materials be present in the ratio of $y$, but this monomer ratio must be maintained throughout the course of the polymerization by continuous addition of the more reactive component.

*Experimental Data*—The copolymerization equation

$$\frac{d[M_2]}{d[M_1]} = \frac{[M_2]}{[M_1]} \cdot \frac{r_2[M_2] + [M_1]}{r_1[M_1] + [M_2]}$$

although it neither requires nor yields any information about rates, provides a quantitative means of comparing the behaviour of monomers in copolymerizations.

Its development assumes that the reactions of the growing radicals with monomers depend only on the monomer units which form the free ends of the growing chains and on the relative monomer concentrations. From a knowledge of the experimentally determined monomer ratio in the polymer, together with the initial composition of the mixture, the reactivity ratios $r_1$ and $r_2$ may be determined. This supplies a quantitative measure of the relative rate of reaction, with a different monomer, of any radical occurring in a given polymer. For example, the reaction of a styrene radical with a series of monomers will give a set of $r_1$ values, all of which are quotients of a common dividend, the rate constant of a styrene type radical with styrene. If the values of $r_1$ are not dependent on the reaction medium, then the rate constant of the reaction of a styrene type radical with a series of substituted double bond compounds may be measured, although the absolute values are not determined. The latter may be deduced if the absolute value in one case is known. *Figure 15* illustrates some of the results obtained for the copolymerization of styrene with other monomers. The reactivity ratios $r_1$ and $r_2$ derived from these curves are summarized in *Table XV*. These results, which must be regarded as only approximate, show that the rate constant of the reaction of a radical derived from styrene with methyl methacrylate is just twice as large

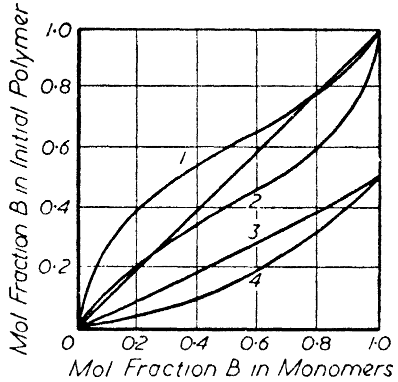


*Figure 15.* *Copolymer composition curves for systems :*

1 *styrene* (A)/*2 : 5-dichlorostyrene* (B)
2 *styrene* (A)/*methyl acrylate* (B)
3 *styrene* (A)/*diethyl chloromaleate* (B)
4 *styrene* (A)/*diethyl maleate* (B)
(*Reference* : 51)

*Table XV*

*Copolymerization of Styrene with Other Monomers*

| *Monomer* $M_2$ | $r_1$ | $r_2$ | *Relative reactivity (temp. 60-70°C)* |
|---|---|---|---|
| *Styrene* . . . . . | — | — | 1·0 |
| *Methyl methacrylate* . . | 0·5 | 0·5 | 2·0 |
| 2 : 5-*Dichlorostyrene* . . | 0·2 | 0·8 | 5·0 |
| *Methyl acrylate* . . . | 0·75 | 0·2 | 1·3 |
| *Diethyl chloromaleate* . . | 2·5 | 0·0 | 0·4 |
| *Maleic anhydride* . . . | 0·04 | 0·0 | 25 |
| *Diethyl maleate* . . . | 5·0 | 0·0 | 0·2 |
| *Acrylonitrile* . . . | 0·37 | 0·05 | 2·7 |
| *Vinylidene chloride* . . | 2·00 | 0·14 | 0·50 |

as the rate constant for its reaction with styrene, whereas with vinylidene chloride it is about half as large as for the reaction with styrene. Taking the rate constant for the reaction of a styrene type radical with styrene as 1·00, and assuming that the rates given in the above are not very dependent on reaction medium or temperature, the relative values of the rate constants for the reaction of eight monomers with the styrene type radical are summarized in the last column of *Table XV*. The values should be regarded as giving the order of magnitude rather than exact values of the reactivity of the same radical towards a set of different monomers.

The data show very clearly the specific nature of the reactivity of free radicals. Similar tables have been compiled for other types of monomer radicals.[52] The order in which the radicals fall is much the same for a number of different reference radicals, even though the absolute rates may vary greatly from one radical to another. The broad conclusion derived from consideration of this tabulation is that styrene, methyl α-chloroacrylate, methyl methacrylate, and methacrylonitrile monomers are very reactive towards chain radicals; acrylonitrile, methylacrylate, and indene are moderately reactive, but vinyl acetate and allyl esters are relatively unreactive. This semi-quantitative generalization is a useful guide to the composition of the copolymer obtained from a mixture of two monomers when not complicated by special selectivity.

The tendency of monomers to show selectivity during copolymerization is shown by certain symmetrically substituted ethylenic derivatives. Thus, maleic anhydride or maleic esters which do not polymerize alone, or at least do so very slowly to low degrees of polymerization, will readily copolymerize with other vinyl monomers and may even accelerate the polymerization rate. The explanation of this apparent anomaly is that such monomers show no measurable tendency to add free radicals of similar structure, but will add readily to free radicals of the ordinary unsymmetrically substituted vinyl type. This may be due to steric or to dipole effects. When a monomer of the maleic ester type copolymerizes with styrene, $k_{22}$ of equation (53) is zero, and the normal set of propagation processes is reduced to three. The composition equation (54) now takes the simple form

$$\frac{[\mathrm{M}_1]_p}{[\mathrm{M}_2]_p} = 1 + r_1 \cdot \frac{M_1}{M_2}$$

The values of $r_1$ for several systems are included in *Table XV*. Furthermore, according to the postulated free radical mechanism, the mol percentage of the maleic derivative in the monomer could not exceed 50 per cent. This has been confirmed experimentally as shown in *Figure 15*.

In the free radical initiated polymerizations so far studied no case has been found in which both $r_1$ and $r_2$ are greater than unity; that is, where each radical prefers to react with the monomer type from which it is derived. Except in special cases, the copolymer will possess a random distribution of the monomer units and will be built up of lengths of sequences of units of the same type. These will be determined by the relative values of the propagation constants. Thus, when $k_{11}$ and $k_{22}$ are large compared with the rate constants $k_{12}$ and $k_{21}$, one would expect to find long sequences of $M_1$'s followed by long sequences of $M_2$'s, whereas if the relative rate constants are reversed, the copolymer will contain short groups of $M_1$'s followed by short groups of $M_2$'s. From probability considerations, ALFREY and GOLDFINGER [49] have shown that if $\bar{n}$ and $\bar{m}$ are the number average lengths of $M_1$ and $M_2$ sequences, and $[M_1]_p/[M_2]_p$ is the ratio of $M_1$ and $M_2$ in the polymer, then these quantities are related by the expression

$$\frac{\bar{n}}{\bar{m}} = [M_1]_p/[M_2]_p$$

## VI

## POLYMERIZATION IN AQUEOUS SOLUTIONS

In the polymerization of monomers in the pure state or in organic solvents, peroxidic compounds are the most commonly used catalysts. We have already seen that these compounds are ready sources of free radicals, and that in homogeneous systems the rate of polymerization is proportional to the square root of the initiator concentration. The kinetic interpretation of this relationship in terms of the free radical mechanism is that the termination process occurs by mutual saturation of two polymeric radicals. A similar dependence of the rate on catalyst concentration is observed in polymerization in aqueous solutions and in emulsions in which the catalyst is a water soluble peroxidic substance, such as hydrogen peroxide or alkali persulphate. This indicates that the termination is by collision of active molecules and that the steady state assumption is justified.

Recently a number of papers [53] have appeared in which it is shown that the addition of small amounts of reducing agents activates the peroxidic catalysts in aqueous polymerizations. The term ' reduction activation ' polymerization [53c] has been coined for this fairly general effect, the outstanding feature of which, from the practical point of view, is that it enables polymerizations to be performed at much greater speeds, or at lower temperatures than are possible by conventional methods. Recent studies of peroxide catalysed vinyl polymerizations have enabled the general principles of reduction activation to be established.

The most complete and thorough examination of redox systems is that by M. G. EVANS and his collaborators,[54] who measured the polymerization of acrylonitrile, methyl methacrylate, methacrylic acid, methyl acrylate, and styrene in aqueous solution, using ferrous ions and hydrogen peroxide as initiator. This system gave rise to a much more rapid formation of polymer than by use of hydrogen peroxide alone. In the absence of the monomer, the peroxide decomposed according to the Haber–Weiss mechanism [55] with the evolution of oxygen.

$$\begin{array}{lll}
H_2O_2 + Fe^{++} & \longrightarrow & HO^- + OH + Fe^{+++} \quad . \quad . \quad (57) \\
HO \;\; + Fe^{++} & \longrightarrow & HO^- + Fe^{+++} \quad . \quad . \quad . \quad . \quad (58) \\
HO \;\; + H_2O_2 & \longrightarrow & H_2O + HO_2 \quad . \quad . \quad . \quad . \quad . \quad (59) \\
HO_2 \; + H_2O_2 & \longrightarrow & HO \;\; + H_2O + O_2 \quad . \quad . \quad . \quad (60)
\end{array}$$

In the presence of a monomer, the oxygen production was very much reduced or even stopped, owing to reaction of the monomer molecule with the chain carriers.

$$OH + CH_2{=}CHX \longrightarrow HO{-}CH_2{-}\dot{C}HX$$

The opening of the double bond in this way leads to polymerization, which has been shown to occur according to the following reaction scheme:

$$\begin{array}{rcll}
Fe^{++} + H_2O_2 & \longrightarrow & Fe^{+++} + OH^- + OH & . \quad . \quad k_1 \\
HO + M & \longrightarrow & HO{-}M\cdot & . \quad . \quad . \quad . \quad . \quad . \quad . \quad k_i \\
HO{-}M\cdot + M & \longrightarrow & HO{-}M{-}M\cdot & \multirow{2}{*}{\Big\} \quad . \quad . \quad . \quad . \quad . \quad k_p} \\
HO(M)_n\cdot + M & \longrightarrow & HO(M)_{n+1}\cdot & \\
HO(M)_n\cdot + \cdot(M_m)OH & \longrightarrow & HO(M)_{n+m}OH & . \quad . \quad . \quad . \quad . \quad k_t \\
HO(M)_n\cdot + OH & \longrightarrow & HO(M)_nOH & . \quad . \quad . \quad . \quad . \quad . \quad k_{t'}
\end{array}$$

By observing the rate of production of $Fe^{+++}$ by reaction (57) Baxendale and Evans determined the value of $k_1 = 1{\cdot}78 \times 10^9 \exp(-10{,}000/RT)(\text{mol litre}^{-1}\text{sec}^{-1})$ and showed that the result was the same in both the absence and presence of monomer.

Assuming that $k_p$ and $k_t$ are independent of chain length, and employing the stationary state condition, it was shown that for a termination reaction by combination, namely

$$\mathrm{HO(M)_{\mathit{n}}\cdot + \cdot(M)_{\mathit{m}}OH \longrightarrow HO(M)_{\mathit{n+m}}OH}$$

then

$$\log \frac{M}{M_0} = \frac{k_p}{\sqrt{k_1 k_t}} \, . \log(1 + a_0 k_1 t) \quad . \quad . \quad . \quad (61)$$

where $a_0$ is the initial concentration of ferrous ions and is equal to the concentration of the peroxide, and $M_0$ is the initial concentration of the monomer.

For the hydroxyl radical termination reaction

$$\mathrm{HO(M)_{\mathit{n}}\cdot + OH \longrightarrow HO(M)_{\mathit{n}}OH}$$

the corresponding expression was shown to be

$$\frac{1}{M} - \frac{1}{M_0} = \frac{k_1 k_p}{k_{t'}} \, . \, t \quad . \quad . \quad . \quad . \quad . \quad . \quad (62)$$

The experimental results proved that (61) was accurately obeyed and thus that termination reaction was mutual saturation of the growing polymer radicals. The temperature dependence of $k_p/\sqrt{k_1 k_t}$ showed that $E_p - \frac{1}{2}E_t = 5{,}000$ cal/mol, where $E_p$ = activation energy for propagation and $E_t$ = activation energy for mutual termination of radicals. The activation energy for the formation of radicals is 10,000 cal—a much lower value than for radical production from benzoyl peroxide in solution ($E \sim 30{,}000$ cal). This accounts for the occurrence of polymerization at much lower temperatures.

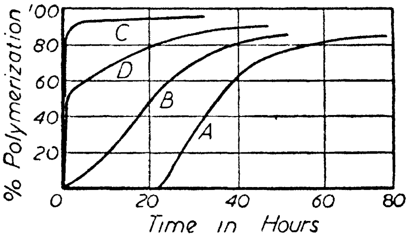


*Figure 16. Polymerization of acrylonitrile in aqueous solution at 20°C*

A *water 100 g,* $(NH_4)_2S_2O_8$ *1·0 g, acrylonitrile 6·45 g; under air*

B *as A but in the absence of oxygen*

C *as A + 0·05 g* $Na_2S_2O_4$

D *as A + 0·05 g hydroquinone*

(*Reference : 53b*)

Many other redox systems have been investigated, but have been found not to be so simple or tangible as the ferrous ion–hydrogen peroxide system. Bacon and Morgan [53] found that, in the persulphate catalysed aqueous solution polymerization of acrylonitrile and styrene, a wide variety of salts, metals and organic compounds act as reduction activation agents of varying efficiency. *Figure 16* illustrates effects of additions to acrylonitrile/persulphate systems.

The interaction between persulphate and an activator, such as thiosulphate, can be described, by analogy with the ferrous/hydrogen peroxide reaction, as follows:

$$\mathrm{S_2O_8^{--} + S_2O_3^{--} \longrightarrow SO_4^{--} + SO_4^{-}\cdot + S_2O_3^{-}\cdot}$$

The radical ions $SO_4^{-}\cdot$ and $S_2O_3^{-}\cdot$ produced react with the monomer and chain polymerization ensues. In fact, the reaction between persulphate ion and a reducing agent may be represented generally as

$$S_2O_8^{--} + R \longrightarrow SO_4^{-}\cdot + SO_4^{--} + R^{+}$$

and the radical ion may react further with water to give hydroxyl radicals

$$\cdot SO_4^{-} + H_2O \longrightarrow HSO_4^{-} + OH$$

Many other electron transfer reactions between the ions may be postulated, and in the presence of a monomer M competing reactions of the following types also occur:

$$\begin{aligned} \cdot SO_4^{-} + M &\longrightarrow \cdot MSO_4^{-} \\ OH + M &\longrightarrow \cdot MOH \\ \cdot S_2O_3 + M &\longrightarrow \cdot MS_2O_3^{-} \end{aligned}$$

Evidence for the occurrence of these reactions is the formation of long chain hydroxyl compounds and sulphates in the emulsion polymerization of ethylene and styrene initiated by persulphate ions and a reducing agent.

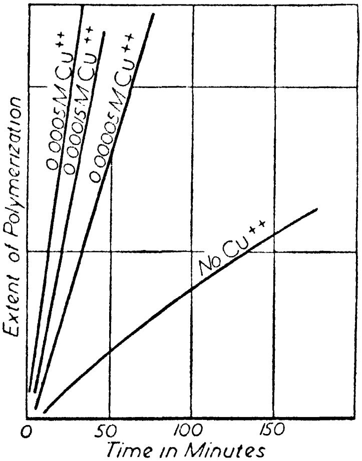


*Figure 17.* Cu$^{++}$ *promoted persulphate/thiosulphate catalysed polymerization of acrylonitrile. Stoichiometric amounts of persulphate and thiosulphate*

(*Reference* : 53*c*)

In the above scheme R may be a metal, or an ion which gives an atom, or a radical ion in the oxidized state; for example

$$S_2O_8^{--} + I^{-} \longrightarrow \cdot SO_4^{-} + SO_4^{--} + I$$

Persulphate ion alone can react in this way, probably owing to the decomposition

$$S_2O_8^{--} \longrightarrow \cdot SO_4^{-} + \cdot SO_4^{-}$$

The remarkable promoting action of the heavy metal ions, silver, copper, ferrous and also of iodide ion, on the persulphate and persulphate/thiosulphate catalysed polymerization of acrylonitrile has been investigated by BACON and MORGAN. By using stoichiometric amounts of persulphate and thiosulphate in an aqueous solution of acrylonitrile at room temperature, MORGAN [53c] showed that the rate of polymerization increased tenfold by the addition of $5 \times 10^{-4}$ mol of cupric ion (*Figure 17*). The actual mechanism of the promoter action of metallic ions and the relative activity of the various radicals, which may be postulated as intermediate steps, are uncertain. The phenomenon is, however, of great practical importance. Thus, the polymerization of styrene or vinyl acetate, catalysed by an organic peroxide, is very slow at room temperature. In aqueous solution or emulsion in the presence of persulphate, a reducing agent and a heavy metal ion, polymerization occurs rapidly at room temperature to give high molecular weight products. The activation energy for peroxide catalysed polymerization is about 23,000–28,000 cal/mol, the value for the corresponding persulphate/thiosulphate reaction is 15,500 cal/mol, and for the silver promoted reaction 12,500 cal/mol.

*Effect of Oxygen*—Polymerizations in aqueous solution and emulsions are retarded by oxygen when catalysed either by a persulphate or by reduction activation systems. Retardation is manifested particularly in the occurrence of an induction period, which varies in length, depending on the oxygen content of the system and the nature of the catalyst. Kolthoff and Dale [56] and Price and Adams [57] observed that air inhibited the emulsion polymerization of styrene and that the length of the induction period was proportional to the oxygen concentration. The oxygen was found to disappear during the induction period, with the production of peroxidic compounds, but no polymerization occurred. The effect of oxygen on the persulphate catalysed polymerization of acrylonitrile in aqueous solution is illustrated in *Figure 16.* These results show that the removal of oxygen reduced the induction period but had no noticeable effect on the rate of polymerization, once polymer formation had begun. In view of the free radical nature of the oxygen molecule, its most probable action in inhibiting the reaction is by combination with the radical involved in the propagation step, thus leading to termination of the chain at an early stage of its growth. Although the addition of reduction activators reduces the induction period, Bacon [53b] concluded that their efficiency was in no way related to their capacity to remove oxygen and that their essential function was not the suppression of oxygen inhibition. There is, however, insufficient data to state unequivocally that the activator functions solely to facilitate radical formation rather than to retard the termination reaction.

# VII
# SUSPENSION AND EMULSION POLYMERIZATION

It is convenient to distinguish polymerization in the pure monomer and in homogeneous solution from that in which the monomer or mixture of monomers undergoes polymerization in a heterogeneous dispersion. Even in the former case, if the solution is not sufficiently dilute, or if the polymer is insoluble in the solvent, a molecularly homogeneous phase at the commencement of the reaction changes to a highly swollen gel as the polymerization proceeds. The polymerization of acrylonitrile in water, or styrene in methanol, are examples of this type. Two types of polymerization in heterogeneous dispersion must be distinguished: *a* suspension and *b* emulsion polymerization.

## SUSPENSION POLYMERIZATION

In this method the monomer is mechanically dispersed in a nonsolvent liquid by stirring or shaking. The initiator may be soluble in the monomer or in the suspending liquid. With this procedure, polymerization takes place in each monomer globule and forms a polymer ' bead ' or ' pearl '; the liquid playing only the role of carrier, assisting agitation and dissipating the heat of reaction without taking any actual part in the change. In only a few cases is the monomer entirely soluble in the carrier liquid (which is most often water) or the initiator insoluble in the monomer but soluble in the water. In such instances some polymerization occurs in the solution phase. This is usually relatively small compared with that in suspension. These considerations show that suspension polymerization may be a complex process but as far as our knowledge goes, the course of the polymerization is almost the same as that observed with the pure monomer phase. A complete review of the results of the polymerization of olefins and diolefins has recently been compiled by HOHENSTEIN and MARK.[58] Quantitative studies by these authors of the polymerization of styrene, dichlorostyrene and methyl methacrylate in water suspension with benzoyl peroxide, potassium persulphate, and sodium perborate as initiators, have shown that the reaction follows essentially the same course as the normal bulk polymerization, with the difference that the polymerizing mass is broken up into small pearls and maintained at constant temperature by the water phase.

In the polymerization of a monomer in water, with a catalyst as the only addition, it is found that, except in a few instances, agglomeration of the particles cannot be prevented by stirring during the ‘ sticky ’ stage of the polymerization. Use is therefore made of suspension stabilizers, or other means to prevent the particles coalescing as the reaction proceeds. Some of the suspension stabilizers which have been used effectively are slightly soluble calcium, magnesium or barium salts, finely divided oxides or silicates, and colloidal organic stabilizers such as gelatine, cellulose derivatives, *etc.* The nature of the suspension stabilizer has no direct influence on the rate of polymer formation.

## EMULSION POLYMERIZATION

This procedure differs from the simple suspension polymerization in that the monomer is either dispersed into droplets which are stabilized by an adsorbed layer of soap molecules, or is solubilized in the soap micelle which is present in aqueous soap solutions. Polymerization may occur in both the droplet and soap micelle phase and also in the water phase, in which most common monomers are soluble even if only to a small extent. From this point of view alone the process may be complicated, and therefore, in any study of the principles of emulsion polymerization, it is necessary to select a simple system, to reduce as far as possible overlapping effects. Besides these interfacial actions, the polymerization proper proceeds *via* a well defined sequence of steps, initiation, propagation and termination, together with possible transfer and branching reactions, and it is vital to an understanding of the heterogeneous polymerization reaction to know precisely the kinetics and location of each elementary process. For example, the locus of the polymerization reaction may be *a* the discontinuous monomer phase; *b* the interface between the monomer and the aqueous phase or *c* the continuous aqueous phase. It is highly probable that in different reactions the locus of the reaction will be different.

*Location of the Individual Reaction Steps*—In their extensive review of emulsion polymerizations, HOHENSTEIN and MARK[59] describe some simple experiments in which monomer vapour is maintained in contact with an aqueous solution of an initiator (perborate or persulphate), and which demonstrate clearly that with a water soluble monomer, polymerization is initiated in the aqueous phase by reaction between monomer and peroxide; the polymer chains precipitate out as soon as they reach a certain length. The interface between monomer and solution, if there is one, does not appear to be a preferred location for activation and propagation. This point of view has been completely substantiated by EVANS and his coworkers in their investigations of aqueous phase polymerization of methyl methacrylate, which has been described previously (page 94). In the presence of a water soluble emulsifying agent, however, the situation is changed significantly. For instance, in the aqueous solution polymerization of methyl methacrylate, initiated by OH radicals, the effect of the addition of the emulsifying agent is to increase both the rate and the extent of polymerization without changing the kinetics of the reaction. The effect of concentration of the emulsifying agent on the rate is shown in *Figure 18*. In terms of the mechanism previously given for this reaction, Evans *et al* regard the termination reaction

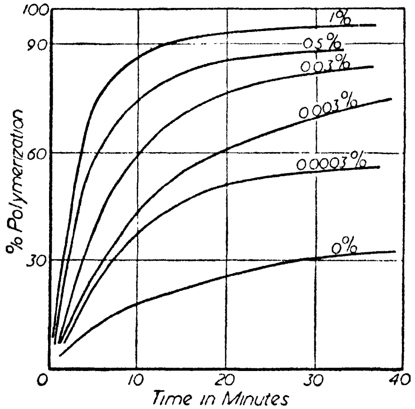


*Figure 18. Effect of varying emulsifying agent concentration on the polymerization of* 0·1 M *aqueous solution of methyl methacrylate at* 25°C

*Initiator* $Fe^{++} + H_2O_2$
$H_2O_2 = Fe^{++} = 10^{-4}M$
(*Reference* : 60)

$$HO(CHX{-}CH_2)_n\cdot + \cdot(CH_2{-}CHX)_mOH \longrightarrow HO{-}(CHX{-}CH_2)_{m+n}{-}OH$$

as analogous to the coagulation of two colloidal particles and the effect of the emulsifying agent as being similar to the effect of protective agents upon colloidal coagulation, thus reducing the termination reaction velocity constant. This constant may thus be regarded as a coagulation constant, and will be a function of the viscosity of the solution and the size of the coagulating particles. The initial rate of polymerization in a concentrated emulsion (using 1–3 per cent cetyl trimethyl ammonium bromide as emulsifying agent) was found to be independent of the change in the amount of non-aqueous phase, and thus of the interfacial area of the emulsion, and was approximately that obtained with the polymerization occurring in the aqueous phase. The monomer was found to disappear from the discontinuous phase more quickly than it polymerized, owing to the polymer chains first formed in the aqueous phase dissolving monomer from the discontinuous phase. In this particular type of system, in which the initiating reaction occurs in solution and the monomer is soluble in the polymer, it appears that the locus of chain growth is a new phase of polymer/monomer solution—a swollen polymer/monomer phase. The qualitative picture of the increase in the rate of polymerization as the reaction proceeds is that the monomer dissolved in the polymer particles reduces the rate of the termination reaction. Since termination involves the migration of active polymer endings towards each other through a highly viscous medium, the condition of viscous diffusion will become the rate-determining factor and $k_t$ will decrease as the viscosity increases. A decrease in $k_t$ would therefore lead to an increase in molecular weight, which is in agreement with experiment.

A different behaviour is observed in the emulsion polymerization of styrene. Using a soap as emulsifying agent and potassium persulphate as initiator, the reaction is characterized by a well defined induction period, after which the rate of polymerization is a linear function of time up to about 80 per cent conversion. The length of the induction period is dependent on the purity of the styrene, but although it may be considerably reduced by carefully purifying the monomer, it has never been completely controlled or eliminated. Extensive investigations[60] have shown that, after the induction period, *a* the rate of reaction is independent of the concentration of emulsified styrene (15–90 per cent conversion) and is best represented by a zero order overall reaction *b* the rate is proportional to the square of the catalyst concentration *c* the activation energy is approximately the same as that of polymerization in solution *d* the average molecular weight is constant during polymerization, as in the solution or bulk reaction. Facts *b*, *c* and *d* indicate that the emulsion polymerization proceeds by a free radical mechanism similar to that in solution. Whereas in the latter case the rate is proportional to the monomer concentration, the peculiarity of the zero order dependence on monomer concentration is determined by some factor not directly connected with the polymerization process. This type of relationship would be expected if the reaction occurs in solution which is being continually replenished by monomer from the discontinuous phase (monomer droplets) at a rate sufficient to maintain the natural propagation rate.

*Action of Modifiers*—In the development of synthetic rubbers by copolymerization of vinyl monomers and dienes in emulsion, it was found that the addition of certain types of organic molecules such as mercaptans, other organic sulphur compounds, or chlorinated hydrocarbons suppressed the formation of gelatinous and partly insoluble polymers, particularly at high conversions. These materials have been termed regulators or modifiers, and their use is of the utmost importance in the commercial production of synthetic rubbers and other polymers. It was at one time thought that these materials prevented the formation of branched and cross linked structures, but many recent and detailed studies[61] have shown that they function mainly as chain breaking agents.

If, in the emulsion polymerization of styrene described in the previous section, 0·5 per cent of dodecylmercaptan (calculated on the weight of monomer) is added to the polymerizing mixture, it produces only a slight effect on the rate, but the viscosity molecular weight is reduced from 265,000 to 15,000. The action is analogous to the effect of carbon tetrachloride on the polymerization of styrene in solution, and the modifier acts as a chain transfer agent; it interferes with the excessive growth of any chains, and thus prevents the formation of large, three-dimensional networks. Other observations on the polymerization of styrene and butadiene with *n*-dodecylmercaptan as modifier[61] showed that the polymers contain approximately one sulphur atom per polymer molecule.

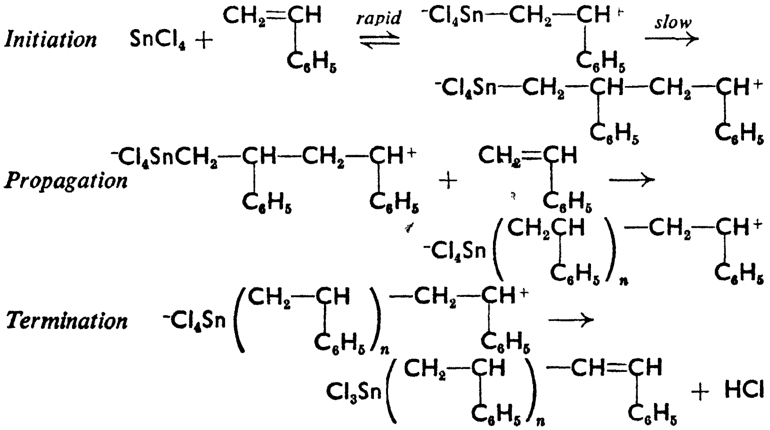
## VIII

## IONIC POLYMERIZATIONS

Up to the present, in our considerations of addition polymerization, we have dealt only with reactions which occur by a free radical mechanism. There are also many catalysed polymerizations which undoubtedly involve ionic intermediates. In spite of the importance of these reactions, their mechanism has not been investigated to anything like the extent of the corresponding free radical reactions. The occurrence of ionic or polar reactions at the carbon–carbon double bond is well known and so well established that it requires no detailed elaboration at this point. Our attention will be confined to such reagents as strong acids, boron trifluoride, aluminium chloride, titanium chloride and stannic chloride, which are very effective in initiating polymerization with certain types of olefinic structures. These polymerizations differ in a remarkable manner from the corresponding free radical reactions. Thus, isobutene will not polymerize under conditions which result in free radical propagation, such as reduction activation, but in the presence of typical Friedel–Crafts catalysts, such as boron trifluoride, aluminium chloride and titanium chloride, the polymerization of liquid isobutene occurs extremely rapidly at temperatures as low as − 120°C, yielding high molecular weight products. The reaction velocity is not apparently decreased by lowering the temperature, but the molecular weight of the polymer is highest when formed at low temperatures. Furthermore, oxygen has no retarding effect, in sharp contrast to its action in free radical reactions. An important feature of the isobutene reaction is the lack of reproducibility (see later). This has been explained by the requirement of a third substance in the reaction (which may be water), which seems necessary for the effective action of the catalyst. Styrene polymerizes readily at room temperature with a stannic chloride catalyst. In contrast to the benzoyl peroxide catalysed reaction, which, like the uncatalysed reaction, has an activation energy of about 24,000 cal, the use of a stannic chloride catalyst reduces the activation energy to less than 3 kcal.[62]

The published data on ionic polymerization are sparse and not always consistent. Although ample qualitative evidence exists, there is a lack of quantitative kinetic data. Most of the useful information relates to the two systems, styrene and isobutene, previously mentioned.

*Styrene and α-Methyl Styrene*—WILLIAMS[62] found that boron trifluoride, stannic chloride and antimony pentachloride gave relatively low molecular weight products (2,500–4,000) at 25°C and that polymerization was at least $10^4$–$10^5$ times faster with antimony pentachloride than with boron trichloride. In carbon tetrachloride the rate with stannic chloride was about $10^3$ times faster than with boron trichloride. The stannic chloride reaction showed an induction period, and was poisoned by HCl and by styrene dimer. The rate of monomer consumption was found to be proportional to the first power of the catalyst and the third power of the monomer concentrations. This result has been explained by PRICE[63] on the basis of the following sequence of reactions.



Assuming that a steady state is set up, the observed law of the dependence of the rate on catalyst and monomer concentrations may be deduced. However, the theoretical relationship must be accepted with some reserve until fuller investigation of the reaction has been carried out. The observed presence of an induction period and the inhibition of the reaction by added hydrogen chloride may have an important influence on the mechanism, since hydrogen chloride may be formed during the reaction.

The exact nature of the intermediate complex of the stannic chloride and the olefin may be different from that postulated, and may be regarded as an association complex with the $\pi$ electrons of the double bond. The formation of such complexes with these catalysts is well established, and it has been shown that the function of inorganic halides in the Friedel–Crafts type of reaction involves the formation of an ionic complex

$$\mathrm{RCl} + \mathrm{AlCl_3} \longrightarrow \mathrm{R^+AlCl_4^-}$$

The reaction with the olefin in the presence of a molecule RY and catalyst may be the coordination of hydrogen or other cation with the double bond

$$\begin{aligned}\mathrm{RY} + \mathrm{AlCl_3} &\longrightarrow \mathrm{R^+AlCl_3Y^-}\\ \mathrm{R^+} + \mathrm{CH_2{=}CHX} &\longrightarrow \mathrm{RCH_2{-}CHX^+}\end{aligned}$$

or

$$\begin{aligned}\mathrm{HCl} + \mathrm{AlCl_3} &\longrightarrow \mathrm{H^+{\cdot}AlCl_4^-}\\ \mathrm{H^+} + \mathrm{CH_2{=}CHX} &\longrightarrow \mathrm{CH_3{-}\overset{+}{C}HX}\end{aligned}$$

The chain termination may then be the reaction between oppositely charged ions, as postulated by POLANYI *et al*[64]; for example

$$\mathrm{R{-}CH_2{-}CH_2^+} + \mathrm{AlCl_4^-} \longrightarrow \mathrm{R{-}CH_2{-}CH_2Cl} + \mathrm{AlCl_3}$$

The polymerization of styrene in thymol has been observed to be third order with respect to styrene concentration.[65] In view of this fact, together with the low molecular weight of the product, it was concluded that the polymerization was of the ionic type. More extensive investigations by WALLING[66], using phenolic solvents, show that the uncatalysed reaction is most probably of the normal free radical type, inhibited by the phenolic solvent. Assuming that this inhibition takes place through chain transfer, yielding unreactive solvent radicals, the third order law may be explained without the assumption of ionic intermediates.

Direct evidence for the ionic mechanism of the stannic chloride catalysed polymerization of $\alpha$-methyl styrene was provided by PEPPER,[67] who showed that both the initial rate and the degree of polymerization were increased by increase of the dielectric constant of the solvent. A similar increase in rate is well established in simple ionic reactions. *Figure 19* shows the plot of the initial rate at 25°C against the dielectric constant of the solvent. The change in number average molecular weight is also indicated on the graph. Since the degree of polymerization $\overline{DP}$ is determined by the ratio of the propagation to the termination reaction $(k_p/k_t)$, an increase in $\overline{DP}$ can be secured either by an increase in $k_p$ or by a decrease in $k_t$. If the propagation step is the reaction of a monomer with an active ionic species, then by analogy with simple reactions between ions and neutral molecules we should expect $k_p$ to be reduced by an increase in dielectric constant. The observed result must therefore be due to a decrease in $k_t$. This may be explained if the termination process is the reaction of a positive active ionic species with one with a negative charge, since the reaction between ions of opposite sign is reduced by increase in dielectric constant.

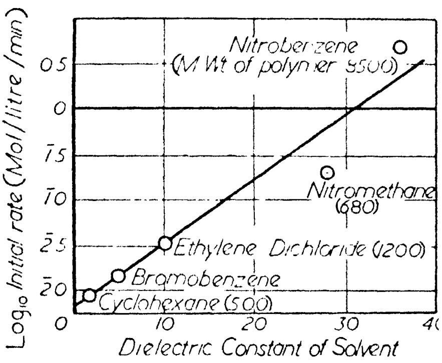


*Figure 19. Variation of initial rate of polymerization of α-methyl styrene with dielectric constant of solvent*

(*Reference* : 67)

*Isobutene*—A detailed investigation of the polymerization of isobutene by Friedel–Crafts catalysts has been carried out by POLANYI and his collaborators.[68] It was found that at –78°C the activity of the catalyst decreased over a wide range down the series $BF_3$, $AlBr_3$, $TiCl_4$, $TiBr_4$, $BBr_3$ and $SnCl_4$, the reaction time varying from a few seconds with $BF_3$ to days with the weakest of the catalysts, $SnCl_4$. With boron trifluoride as catalyst it was concluded that a third component was essential in order that the process may take place at an appreciable rate. HCl and HF are inhibitors. In the case of titanic chloride the 'activator' has been identified as water, which, in conjunction with titanic chloride, can act as a chain starter. The following possible mechanism, involving an acid hydrate, was proposed[64]

*Initiation*

$$TiCl_4 + H_2O \longrightarrow TiCl_4{\cdot}H_2O$$

$$TiCl_4{\cdot}H_2O + M \longrightarrow MH^+ + TiCl_4OH^-$$

*Propagation*

$$MH^+ + M \longrightarrow M_2H^+$$

$$M_nH^+ + M \longrightarrow M_{n+1}H^+$$

*Termination* $M_{n+1}H^+ + TiCl_4OH^- \longrightarrow M_{n+1} + TiCl_4{\cdot}OH_2$

*or* $\longrightarrow M_{n+1}{\cdot}HOH + TiCl_4$

According to this scheme, the efficiency of titanic chloride as catalyst in initiating polymerization is dependent upon the acid strength of the $TiCl_4{\cdot}OH_2$ complex. If this scheme is generally applicable to Friedel–Crafts polymerization of isobutene, then the activity of the catalysts would be proportional to the acid strengths of their hydrates. Independent measurements [68] have shown that acid strengths of strong catalysts are markedly greater than those of weaker catalysts.

Hydrogen chloride is ineffective as an activating agent with $TiCl_4$, which seems to indicate that the equilibrium reaction at low temperatures

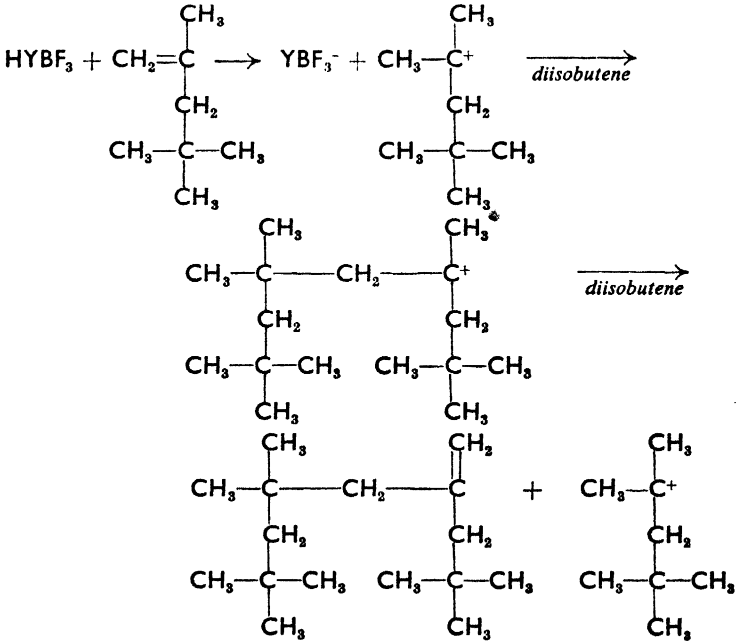
$$TiCl_4 + HCl \rightleftharpoons TiCl_5^- + H^+$$

is very much displaced to the left, compared with

$$TiCl_4 + H_2O \longrightarrow TiCl_4OH^- + H^+$$

This may not be so at higher temperatures.

The dimer of diisobutene $C_8H_{16}$, in the presence of $BF_3$ yields no products higher than $C_{16}H_{32}$, owing to the fact that polymerization is prevented by steric hindrance. By analogy with isobutene it may be assumed that this initial reaction is


HYBF₃ + CH₂=C(CH₃)–CH₂–C(CH₃)₃ ⟶ YBF₃⁻ + CH₃–C⁺(CH₃)–CH₂–C(CH₃)₃
diisobutene
diisobutene
+

Further addition is prevented (as may be most easily seen from a model) by steric hindrance between the methyl group of adjacent monomer units. The carbonium ion reacts further with a monomer molecule by proton transfer according to the above reaction scheme, and initiates a proton chain which never goes beyond the dimerization stage.

*Vinyl Ethers*—The stannic chloride catalysed polymerization of *n*-butyl vinyl ether possesses certain novel features which have not yet been fully explained. ELEY and PEPPER[69] found that the reaction could proceed with explosive vigour at room temperature. The reaction was characterized by an induction period (which was not due to impurities), during which short chains were formed. This was followed by an accelerating reaction and, in sharp contrast to free radical polymerizations, the molecular weight of the polymer increased as the reaction progressed. The initiation reaction was shown to be most probably the formation of an ionic complex with the ether. Each stannic chloride molecule was shown to initiate a large number of chains, and it was assumed that the chain termination reaction was the spontaneous release of a $SnCl_4$ molecule from the chain, which could then activate further monomer molecules.

In their recent work ELEY and RICHARDS[70] find that the stannic chloride catalysed polymerization of vinyl 2-ethyl hexyl ether is slower than that of vinyl butyl ether and can be measured under isothermal conditions. The reaction velocity, in regard to its dependence on both catalyst and monomer concentration, may be accurately described by the kinetic scheme proposed for the vinyl ether polymerization when treated by the usual stationary state method. These authors have also investigated the catalytic action of iodine, initially described by CHALMERS[71] in the polymerization of vinyl ethers. The results indicate that this reaction is of the ionic type.

## IX

## ELECTRONIC STRUCTURE OF THE DOUBLE BOND AND POLYMERIZATION

Starting from the most elementary viewpoint, the activation energy for chain initiation is the energy required to form a radical or ion from the monomer. In our previous considerations it has been sufficient to regard the initiator as a substance which opens the double bond. The activation of the double bond may be more satisfactorily expressed in terms of the modern view of the electronic structure of the bond. This treatment provides a more precise representation of the polymerization process and a satisfactory correlation of the kinetic data.

The normal carbon atom has two paired 2*s* and two unpaired 2*p* electrons in its outer shell. In carbon compounds the atom is in an excited state in which one *s* and three 2*p* electrons all have unpaired spins. The wave functions representing these electrons are known as electron orbitals. Chemists have long known that in methane, for example, the four CH bonds are all equal and arranged tetrahedrally. The answer to this apparent anomaly is that the *s* and *p* electron orbitals mix up or combine, and this so-called hybridization of the *s* and *p* orbitals leads to the strongest bonds, at tetrahedral angles with each other. When a carbon atom takes part in double bond formation it appears that one *s* and two *p* orbitals hybridize to form three trigonal bonds which lie at 120° with each other in a plane. The fourth orbital retains its *p* character unchanged. When the two carbon atoms are joined by a double bond, one of the linkages is formed by the overlapping of one of the trigonal orbitals of each atom, whilst the second linkage results from the pairing of the two unchanged *p* orbitals. The first of the two linkages making up the double bond is referred to as a $\sigma\sigma$ bond and has the characteristics of a normal single bond. The second linkage is known as a $\pi\pi$ bond and is of a different character. The double bond thus consists of one $\sigma\sigma$ and one $\pi\pi$ bond. The latter is much weaker than the former. The $\sigma\sigma$ bond is symmetrical, and thus free rotation can occur around it. The situation is different with the $\pi\pi$ bond. Since the two *p* orbitals tend to overlap as much as possible to give the strongest bond, any rotation causes an increase in potential energy, and thus for rotation to occur energy must be supplied from outside. The $\pi\pi$ electrons are often referred to as unsaturation electrons and are responsible for the characteristics of the double bond.

EYRING and HARMAN[72] have carried out a theoretical treatment of the energy states of the double bond. The estimated energies of the unsaturation electrons are shown in *Figure 20*, the energy being given as a function of the angular rotation of one methylene group with respect to the other. In the lowest state *N*, both electrons occupy the same bonding orbital, and so, by Pauli's Principle, must have anti-parallel spins; thus state *N* is a singlet state. On excitation, one electron is promoted to a non-bonding orbital, so that two states are now possible, dependent on whether the spins are paired or unpaired—*viz* a singlet state *V* and a triplet state *T*. It will be observed that the triplet state is close to the ground state. The higher singlet state is the one responsible for ultraviolet absorption at 1,800 Å. In addition to these states, there is another, *N′*, in which both unsaturation electrons are in anti-bonding orbitals, and as one methylene group rotates, *N′* becomes lower and lower in energy, so that at $\phi = 180°$ it becomes the ground state. Similarly, the state *N* increases in energy on rotation so that at $\phi = 180°$ it plays the same role that *N′* played at $\phi = 0°$. At $\phi = 90°$, the point where *N* and *N′* have equal energy, resonance occurs, as indicated by the dotted curves. The state *N′* is ionic in nature, and by interreaction with the homopolar state *N*, enters very largely into the lowest singlet state at $\phi = 90°$. This state is considerably lower in energy than the polar singlet state, *V*. Thus, the ground state is made up of polar and homopolar contributions, whereas the triplet state is purely homopolar. Transition to state *T* involves uncoupling of the spins of the unsaturation electrons, and gives rise to 'internal radical formation'. This transition requires a magnetic field, and since the internal field of the molecule is weak, the transition will rarely occur in an isolated molecule, even if it possesses the necessary energy. In the presence of atoms, radicals or molecules containing an odd electron, the uncoupling is probable, and would be expected to occur when an odd molecule came within the kinetic radius of the ethylene.

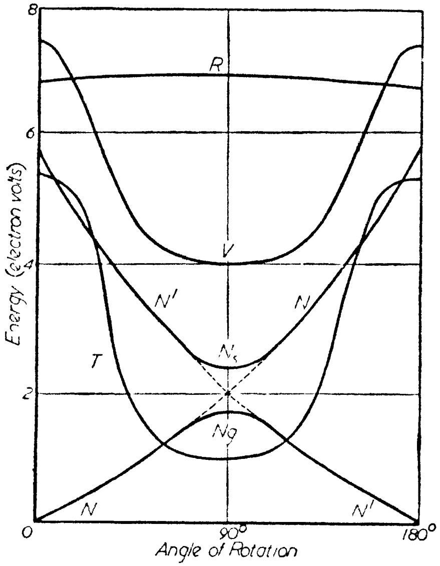


*Figure 20. Schematic diagram of the energy levels in ethylene*
(*Reference* : 39)

We thus see that reactions can go through two mechanisms by excitation to *a* $T_g$, a triplet state, and *b* $N_g$, an ionic state, both of which are not far above the ground state. One can speak of these reactions as following a free radical or an ionic mechanism. That two such mechanisms exist has been clearly established by MAGEE Jr., SHAND and EYRING,[73] after consideration of the known data on *cis–trans* isomerization. They find that the results fall into two groups. The first are those with an activation energy of about 42 kcal/mol and a frequency factor $\sim 10^{11}$. In the second class are those isomerizations with an activation energy of ~23 kcal/mol, and a low frequency factor $\sim 10^{4}$. Those in the first group isomerize by rotation against the high energy barrier of the normal state of ethylene, the top of which must be placed at about 42 kcal. Reactions in the second class are supposed to proceed adiabatically from state $N$ to state $T$ at the crossing point of the potential energy curves of the two states. This requires an activation energy of 23 kcal. The probability of transmission from the singlet to the triplet state is, however, very low, and this accounts for the low observed frequency factors.

*Table XVI*

*Rates of Polymerization*

| *Compound* | *Temperature* °C | *Catalyst* | *Pressure* | *Frequency factor cc/mol sec* | *Activation energy kcal* |
|---|---|---|---|---|---|
| *Ethylene* (g) | 350–500 | | 2·5–10 atm | $10^{10}$ | 35·0 |
| " | 377–393 | | 1420 mm | $4 . 10^{12}$ | 43·5 |
| " | 358–414 | | 10 atm | $10^{12·8}$ | 42·7 |
| *Propylene* (g) | 330–400 | | Sealed tube | $10^{11·45}$ | 37·4 |
| *Isobutene* (g) | 330–400 | | " | $10^{13·6}$ | 43·0 |
| 2 : 3-*Dimethyl butadiene*-1 : 3 (g) | 309–398 | | 160–195 mm | $1·4 . 10^{10}$ | 25·3 |
| *Cyclopentadiene* (g) | 120–160 | | 373–1880 mm | $8·5 . 10^{7}$ | 14·9 |
| *Chloroprene* (l) | 40– 50 | | — | $10^{9·45}$ | 20·2 |
| *Styrene* (l) | 100–132 | *None* | — | $7·5 . 10^{5}$ | 28·6 |
| " | 27– 50 | *Benzoyl peroxide* | — | $6 . 10^{12}$ | 29·3 |
| " | 50– 60 | $(C_6H_5)_2C(NC)\cdot$ | — | $10^{12·2}$ | 23·5 |
| d-s-*Butylchloracrylate* (*dioxane solution*) | 26– 68 | *Benzoyl peroxide* | — | $10^{7·7}$ | 15·2 |
| *Indene* (l) | 120–188 | | — | $10^{6·85}$ | 26·0 |
| " (*toluene solution*) | 120–200 | | — | $10^{4·6}$ | 20·0 |
| *Isoprene* (l) | 100–150 | | — | $10^{2·8}$ | 18·8 |
| " | 154–160 | | 1000 atm | $10^{4·84}$ | 17·0 |
| *Butadiene* (l or g) | 150–200 | | — | $10^{9·8}$ | 25·0 |
| " (l) | 100–150 | | — | $10^{3·8}$ | 13·0 |

An examination of the data on the rates of dimerization of olefins and alkyl-substituted olefins, and on the rate of initiation of polymerization, revealed a similar classification.[39] The former require activation energies of the order of 40 kcal, whereas the polymerization reactions (*Table XVI*) fall into the second group. The frequency factor is low for the uncatalysed reactions, but is normal for those catalysed by free radicals.

The catalysis of the polymerization of styrene by benzoyl peroxide does not occur with any significant change in the activation energy. This would be the case if the activation in both the catalysed and uncatalysed reaction is the excitation from the singlet to the triplet state. The transmission coefficient for the passage through the triplet state is very low unless facilitated by some form of interaction, and this is reflected in the low frequency factor of the uncatalysed reaction. EYRING and his collaborators [39] assume that the benzoyl peroxide forms a molecular complex with the styrene, in which it exerts sufficient interaction to facilitate the transition to the triplet state. The triplet complex then decomposes into free radicals. This may be formulated

$$\mathrm{A} + \mathrm{B} \underset{k_{a'}}{\overset{k_a}{\rightleftharpoons}} (\mathrm{AB})_t$$

$$(\mathrm{AB})_t \xrightarrow{k_b} \mathrm{A}^* + \mathrm{B}$$

The velocity of initiation is given by

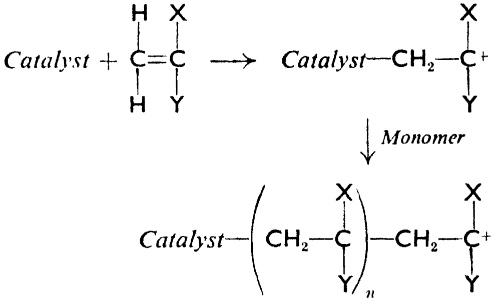
$$V_{init} = \frac{k_a k_b [\mathrm{A}][\mathrm{B}]}{k_{a'} + k_b}$$

as required by experiment.

An alternative explanation is that the benzoyl peroxide gives radicals which are the initiating catalysts. Whilst there is no doubt that radicals are the true initiating catalysts in many reactions, recent evidence [74] indicates that complexes formed between benzoyl peroxide with the monomers of styrene and vinyl acetate may be important in thermal polymerizations.

Examination of the states of the ethylene molecule (*Figure 20*) show that polar states contribute to the ground state, and thus the electronic structure also suggests a mechanism for polar addition. Calculation shows that as one methylene is rotated with respect to the other, the bond between the unsaturation electrons weakens and the polar state contributes more and more to the lowest state of the molecule.

Now, catalysts like $\mathrm{AlCl_3}$ or $\mathrm{SnCl_4}$ have a strong affinity for electrons, and thus will readily form a bond with the unsaturation electrons of the double bond, stabilizing them on one carbon atom. The reaction may be formulated



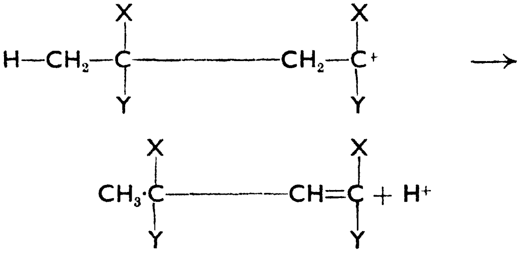
$$\text{Catalyst} + \overset{\text{H}}{\underset{\text{H}}{\text{C}}}=\overset{\text{X}}{\underset{\text{Y}}{\text{C}}} \longrightarrow \text{Catalyst}-\text{CH}_2-\overset{\text{X}}{\underset{\text{Y}}{\text{C}}}{}^{+}$$

$$\Big\downarrow \text{Monomer}$$

$$\text{Catalyst}-\left(\text{CH}_2-\overset{\text{X}}{\underset{\text{Y}}{\text{C}}}\right)_n-\text{CH}_2-\overset{\text{X}}{\underset{\text{Y}}{\text{C}}}{}^{+}$$

Since the polymer formed is in the ionized state, growth can occur with little activation energy, as long as this condition is maintained.

Stabilization of the chain requires the loss of the catalyst from one end and rearrangement to give a double bond. For example, if the catalyst is a proton, then



$$\text{H}-\text{CH}_2-\overset{\text{X}}{\underset{\text{Y}}{\text{C}}}\text{------}\text{CH}_2-\overset{\text{X}}{\underset{\text{Y}}{\text{C}}}{}^{+} \longrightarrow$$

$$\text{CH}_3\cdot\overset{\text{X}}{\underset{\text{Y}}{\text{C}}}\text{------}\text{CH}=\overset{\text{X}}{\underset{\text{Y}}{\text{C}}} + \text{H}^{+}$$

The fact that many substances give only short chains can be attributed to the speed with which rearrangement occurs in competition with addition. Long chains will be favoured at low temperatures, provided the activation energy for termination is greater than that of chain growth.

## APPENDIX

Recently a modified method for the experimental determination of the absolute velocity constants of vinyl polymerizations has been described by BAMFORD and DEWAR (Faraday Society Discussion: ‘Labile Molecule’, Oxford, September 1947. *Proc. roy. Soc. A* (In press).) On cutting off the light in a photochemically initiated polymerization the rate does not fall immediately to the dark value. The theory of this after-effect, which may be measured by viscosity change, provides a fourth relationship necessary for the determination of the individual constants. The authors observe the same general features as previously reported by Melville and Bartlett, namely a low temperature independent factor for the chain propagation step. With styrene they find a small activation energy of 3 kcal for the termination reaction.

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## CHAPTER 4

# THERMODYNAMICS OF SOLUTIONS OF HIGH POLYMERS

IN THEIR BEHAVIOUR towards solvents, large molecules exhibit very characteristic properties. Whereas low molecular weight substances dissolve in a suitable solvent to a well defined saturation limit, a polymer in one solvent may merely imbibe liquid and swell without going into solution, yet the same material in a better solvent will disperse completely. As a rule, the solubility decreases with increase in molecular size. Cross linking of the chains also decreases the solubility, and network structures are either completely insoluble, or may show limited swelling. Another property of chain polymer solutions, which shows remarkable deviations from the normal behaviour of simple liquids or solutions, is their abnormally high viscosity. The cause of these differences is that the properties of the solution are dependent upon the size and configuration of the dissolved molecules. Conversely, from a knowledge of the laws of behaviour of polymer solutions, it is possible to derive information about the shape and dimensions of the dispersed molecules.

The properties of polymer solutions must, of course, be governed by the same fundamental laws as are applicable to solutions of smaller molecules. The effects of size and shape give rise to new phenomena characteristic of large molecules and, as a consequence, the fundamental laws need modification and amendment to include these effects. In this chapter we shall consider the general properties of polymer solutions and the theories which have been developed to explain the observed experimental results.

## I

## EQUILIBRIUM PROPERTIES OF HIGH POLYMER SOLUTIONS

The first group of properties in which we are interested is concerned with two phases which are in equilibrium, one or both of which may be a solution of the polymer. For example, *a* the pressure of the solvent vapour in equilibrium with a polymer solution, *b* the freezing point, in which the solid phase in equilibrium with the solution usually consists of the pure solvent, *c* the osmotic pressure of a solution, *d* solubility and swelling equilibria.

Each of these equilibria can be examined by the rigorous methods of thermodynamics and statistical mechanics. The well known laws which may be deduced for solutions of small molecules, and which relate an experimentally measurable property with a property of the solvent in solution (for example, Raoult's or Henry's law), do not, in general, hold for solutions of high molecular weight materials. It is therefore desirable first of all to look into the causes of these deviations and to deduce the modified laws applicable to such solutions.

In order to give a complete thermodynamic description of a simple binary system—polymer/solvent—it is necessary to formulate expressions for the volume, free energy and heat content of a solution in terms of composition, temperature and pressure. Our aim is to seek the nature of these dependences and, if possible, to formulate them in a quantitative manner. It may be well if we begin by summarizing certain well known thermodynamic relationships which are applicable to solutions.

The condition for equilibrium between a solution containing a given component, and another phase—whether it be vapour, solid, liquid or solution—is that the partial free energy of the component must be the same in every phase present. This condition leads to a number of well known relationships.

If we consider the isothermal transfer of one mol of liquid from a mass of pure liquid of vapour pressure $p_1^0$ to an infinite amount of solution above which the vapour pressure of the liquid is $p_1$, the resultant changes in the Gibbs free energy, entropy and heat content, $\Delta G_1$,* $\Delta S_1$, $\Delta H_1$, are termed the ' Gibbs Free Energy of Dilution ', the ' Entropy of Dilution ' and the ' Heat of Dilution ', respectively. It may be shown that these quantities are related by the following generalizations:

*1* The change of vapour pressure is given by

$$\Delta G_1 = RT \ln \frac{p_1}{p_1^0} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

*2* The vapour pressure is related to the lowering of the freezing point by the equation

$$\ln \frac{p_1^0}{p_1} = \frac{L_f}{RT_f^2} \cdot \theta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

---

* The notation *G* for the Gibbs Free Energy is that recommended by a joint committee of the Chemical, Faraday and Physical Societies, and is used in recent British papers. The equivalent symbol *F* is employed by American writers.

where $L_f$ = molar latent heat of fusion of solvent
$T_f$ = freezing point of pure liquid solvent
$\theta$ = freezing point depression produced by the solute.

*3* The osmotic pressure, $\Pi$, of a solution is related to the vapour pressure of the solvent and solution according to

$$\Pi \bar{V}_1 = RT \ln \frac{p_1^0}{p_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $\bar{V}_1$ = partial molar volume of the solvent in the solution, and thus from (1)

$$\Delta G_1 = -\Pi \bar{V}_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The properties of a solution cannot be related, by purely thermodynamic argument, to the concentration of the components in solution. When, however, the variation of one of these properties with concentration is known, the others can be calculated by thermodynamic methods. A study of the behaviour of solutions has shown that generalizations can be introduced which are believed to be universally valid for dilute solutions. These generalizations may be stated in several ways, but the one of present interest is Raoult's law, which may be expressed as

$$\frac{p_1^0 - p_1}{p_1^0} = N_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

or

$$\frac{p_1}{p_1^0} = N_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where $N_1$ and $N_2$ are the molar fractions of solvent and solute respectively.

Thermodynamics also gives us the well known relationship between the entropy of dilution and the free energy and heat of dilution

$$\Delta G_1 = \Delta H_1 - T\Delta S_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The heat of dilution is determined by the temperature coefficient of the free energy according to the relationship

$$\Delta H_1 = \left[\frac{\delta(\Delta G_1/T)}{\left(\frac{1}{T}\right)}\right]_{P,\, n_2} = -\frac{RT^2}{m_1}\left(\delta \ln \frac{p_1}{p_1^0}\Big/\delta T\right)_{P,\, n_2} \quad . \quad (8)$$

When $\Delta H_1 = 0$, equation (7) reduces to

$$\Delta G_1 = -T\Delta S_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Solutions obeying this law are called 'ideal' solutions. In his treatment of solution, HILDEBRAND[1] accepts Raoult's vapour-pressure equation as the definition of an ideal solution, and hence for such a solution it follows from equations (1), (6) and (9) that

$$\Delta\bar{G}_1 = \bar{G}_1 - \bar{G}_1{}^0 = RT \ln N_1 \quad . \quad . \quad . \quad (10)$$

$$\Delta\bar{S}_1 = \bar{S}_1 - \bar{S}_1{}^0 = -R \ln N_1 \quad . \quad . \quad . \quad (11)$$

where $\bar{G}_1$ = partial molal free energy of the solvent in solution
$\bar{G}_1{}^0$ = partial molal free energy of the pure liquid solvent
$\bar{S}_1$ and $\bar{S}_1{}^0$ are the corresponding entropies.

Equations (10) and (11) apply only to extremely dilute solutions. At lower dilutions, where the solutions are no longer ideal, the partial molal free energies may be expressed in terms of their activities, which are defined by the relation

$$\Delta\bar{G}_1 = \bar{G}_1 - \bar{G}_1{}^0 = RT \ln a_1 \quad . \quad . \quad . \quad (12)$$

where $a_1$ is the activity of the solvent.

Raoult's empirical law is true when $a_1 = N_1$. Therefore the condition for an ideal solution to exist is that the heat of mixing of the two components in the liquid form be zero and that the entropy of solution has the ideal value given by equation (11). Any deviation from ideality may be due either to the heat of dilution not being equal to zero, or the entropy of dilution not being given by $-R \ln N_1$. Both of these factors, of course, may be operating together.

High polymer solutions show large deviations from ideal behaviour, and it will be shown that the deviation is largely due to the entropy change rather than to the occurrence of a non-zero heat of dilution.

## ENTROPY OF MIXING

It may be shown theoretically that Raoult's law, which has been assumed to be valid for dilute solutions, is only strictly true for mixtures of molecules of the same size. It is interesting to deduce this result, because the theoretical treatment of mixtures of small and large molecules is a direct extension of this simple calculation, and the method provides a clear picture of the causes of deviations from ideality in the latter systems.

Suppose that we have a system of $m_1$ molecules of type A and $m_2$ molecules of type B. If we determine the number of distinguishable ways, $w$, in which the molecules can be arranged to form a given mixture, then by a well known theorem in statistical mechanics the entropy of mixing, $\Delta S$, is given by

$$\Delta S = k \ln w \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

where $k$ = Boltzmann constant.

We will suppose that the molecules of types A and B are sufficiently similar in size for one to be substituted for the other without causing any other change in the solution. We regard the solution as built up from $m_1$ and $m_2$ sites arranged regularly as a lattice, each site being capable of accommodating either type of molecule. The number of ways of arranging $m_1$ and $m_2$ molecules on the lattice is $(m_1 + m_2)!$, and thus the entropy of the assembly is $k \ln (m_1 + m_2)!$. This is the entropy of random mixing of $m_1$ molecules of type A with $m_2$ molecules of type B. If the $m_1$ molecules were separated, then, since they are all alike and indistinguishable, the number of ways of arranging $m_1$ molecules on $m_1$ lattice points is $m_1!$. A similar argument applies to $m_2$ molecules. Therefore the entropy of the system of separated molecules is $k \log m_1!m_2!$. Hence the entropy increase on mixing is

$$\begin{aligned}\Delta S_m &= k \ln (m_1 + m_2)! - k \ln m_1!m_2! \\ &= k \ln \frac{(m_1 + m_2)!}{m_1!m_2!} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)\end{aligned}$$

Using Stirling's Theorem for large values of the $m$'s—

*viz* $\ln m_1! = m_1 \ln m_1 - m$, equation (14) becomes

$$\Delta S_m = -k\left\{m_1 \ln \frac{m_1}{m_1 + m_2} + m_2 \ln \frac{m_2}{m_1 + m_2}\right\} \quad . \quad (15)$$

or, using molar quantities,

$$\frac{m_1}{N_0} = n_1 \quad \text{and} \quad kN_0 = R$$

$$\Delta S_m = -R\{n_1 \ln N_1 + n_2 \ln N_2\} = n_1\bar{S}_1 + n_2\bar{S}_2 \quad . \quad (16)$$

which would be the expression for the entropy of mixing if Raoult's law were obeyed. This relationship has been found to be fairly well obeyed for mixtures of low molecular weight liquids. It is immediately evident that the expression will be inapplicable to a mixture of polymer molecules and solvent molecules, since the former may be many hundreds of times the size of the latter, and the assumption that a lattice point can accommodate either a solvent or a polymer molecule is entirely ruled out. Even when one of the molecules is just twice the size of the other, calculation shows that the activity coefficient arising from the entropy of mixing is 0·7 to 0·8. Employing the same idealized lattice model, MEYER[2] suggested that similar calculations for the entropy of mixing long chain molecules with small molecules could be made by computing the number of ways of arranging a flexible chain on an array of lattice points, in such a way that each site could be occupied either by a solvent molecule, or a segment of the polymer molecule, having a size approximately equal to that of the solvent molecule. The calculation, which was carried out independently by FLORY[3] and HUGGINS,[4] consists in counting the number of ways of placing $N_1$ solvent molecules and $N_2$ solute molecules (each consisting of $n$ submolecules) on $N_1 + nN_2$ sites in the lattice, the entropy being obtained as before by the use of the probability equation, $S = k \log w$. It is normally assumed that the segments are flexibly connected, so that the $(i + 1)$th segment of the chain is free to occupy any of the $z$ cells (where $z$ is the coordination number of the lattice) surrounding the cell occupied by the $i$th segment of the chain, the one occupied by the $(i - 1)$th segment excepted. The calculations are somewhat lengthy, and will not be reproduced here. Both analyses lead to similar equations for the entropy of mixing, $\Delta S_m$. The expression obtained by Huggins, which includes some refinements to the above ideal model, for the partial molal entropy of dilution $\delta(\Delta S_m)/\delta N_1$ is

$$\Delta\bar{S}_1 = -R\left[\ln(1 - v_2) - \left(1 - \frac{1}{n}\right)\frac{z'}{2}\ln\left(1 - \frac{2v_2}{z'}\right)\right]. \qquad (17)$$

where $n$ = number of submolecules equal in size to the solvent molecule, and will normally be equal to the degree of polymerization
$v_2$ = volume fraction of the solute
$z'$ = a corrected coordination number, very nearly equal to $z$.

On series expansion equation (17) becomes

$$\Delta\bar{S}_1 = Rv_2\left[\frac{1}{n} + v_2\left[1 - 2\left(1 - \frac{1}{n}\right)\Big/z'\right]\Big/2 \right.$$
$$\left. + v_2^2\left[1 - 4\left(1 - \frac{1}{n}\right)\Big/(z')^2\right]\Big/3 + \dots\right.$$

When $n$ is large, the equation reduces to the approximate form

$$\Delta\bar{S}_1 = Rv_2\left[\frac{1}{n} + v_2\left(1 - \frac{2}{z'}\right)\Big/2 + v_2^2\left[1 - \frac{4}{(z')^2}\right]\Big/3 + \dots \right. \qquad (18)$$

The corresponding equation for the partial molar entropy of solution $\Delta\bar{S}_2$ is

$$\Delta\bar{S}_2 = Rv_1\left[n + v_1\left(\frac{1}{2} - \frac{n}{z' - 2}\right)\right] \quad . \quad . \quad (18a)$$

MILLER,[5] by a different approach to the calculation, arrived at an expression for $\Delta\bar{S}_1$ practically equivalent to (17); namely

$$\Delta\bar{S}_1 = -R\left[\ln(1 - v_2) - \frac{z}{2}\ln\left\{1 - \frac{2v_2}{z}\left(1 - \frac{1}{n}\right)\right\}\right] . \quad (19)$$

If $n$ is large, Flory's, Huggins's, and Miller's equations reduce to the same expression.

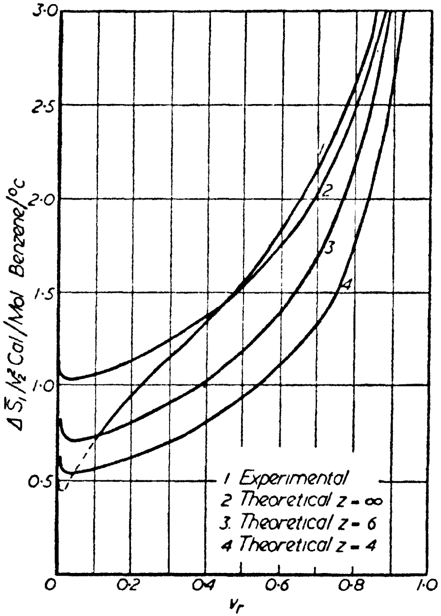

*Figure 21. Entropy of dilution of rubber by benzene*

*(Reference : 6)*

Data for the comparison of the theoretical relationships with experimental results are limited to the system rubber/solvent, since only in this case have systematic measurements over a range of concentrations been completed. *Figure 21* shows the experimental results for the entropy of dilution obtained by GEE and ORR.[6] The free energy of dilution was calculated from vapour pressure measurements by use of the thermodynamic function given in equation (1); the heat of dilution was derived from the temperature coefficient of the vapour pressure according to equation (8) and was also measured directly by a calorimetric method. The entropy of dilution could then be evaluated by the application of the fundamental relationship, $\Delta\bar{S}_1 = (\Delta\bar{H}_1 - \Delta\bar{G}_1)/T$. The theoretical curves calculated from equation (19), taking $z = \infty$, 4 and 6 with $n = 5{,}000$, are represented on the same diagram. It is evident that, although the theory accounts for the order of magnitude of the entropies and does explain in a most satisfactory manner the deviation of polymer solutions from ideality, there remains a considerable discrepancy between the theoretical and experimental curves, particularly at high dilutions. The same conclusion follows if the theoretical expressions of Flory and Huggins are used instead of equation (19). Gee and his coworkers have found similar divergences from theory for rubber solutions in other hydrocarbons and in polar solvents, and it is obvious that amplification and refinement of the existing theory is necessary before it can be regarded as entirely satisfactory.

The theoretical relationships for the entropy of mixing used above were deduced on the assumption that the heat of mixing of the two components was zero. If this is not the case and $\Delta\overline{H}_1 \neq 0$, the attraction between like molecules is either larger or smaller than the attraction between unlike molecules (solvent and polymer), and there will be a tendency towards aggregation or solvation. The heat of mixing of rubber and benzene is positive, and the assumption of random mixing may not therefore be valid. Several attempts to improve the theory have been made by taking into account this departure from random mixing, but detailed calculation has shown that the correction terms in all normal cases are small, and insufficient to account for the observed discrepancies. In their most recent work, Gee and Orr[6] have suggested that the rapid fall-off in $\Delta\overline{S}_1/v_2^2$ with increasing dilution (with a parallel change in $\Delta\overline{H}_1/v_2^2$) is due to the coiling of the rubber molecules in dilute solution giving rise to intramolecular contacts. It remains to be seen how the theory may be extended to include this coiling effect, which may not only apply to rubber molecules, but may be of general significance. The present position would be much more satisfactory if more data were available on other polymer/solvent systems, and no extensive test with general theory will be possible until further experimental results are forthcoming.

## HEAT AND FREE ENERGY OF MIXING

The free energy of mixing of a polymer with a solvent is related thermodynamically to its partial molal heat of mixing and to the entropy of mixing by the relationship

$$\Delta\overline{G}_1 = \Delta\overline{H}_1 - T\Delta\overline{S}_1 \quad . \quad . \quad . \quad . \quad . \quad (20)$$

The entropy term may be evaluated as described above, and hence, in order to give a theoretical expression for $\Delta\overline{G}_1$, it is necessary to formulate an equation for the heat term. Approximate relationships for the partial molal heat of mixing of non-polar liquids have been deduced and found to be satisfactory for regular solutions of small molecules.[1] The relationships for the heat of dilution and solution may be expressed in the form

$$\Delta \bar{H}_1 = A_{12} V_1 v_2^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

$$\Delta \bar{H}_2 = A_{12} V_2 v_1^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

where $V_1$ and $V_2$ are the molar volumes of the solvent, $v_1$ and $v_2$ = volume fraction of the second component in the solution, and $A_{12}$ is a constant related to the molar energies of evaporation of the component.[7] It is to be expected that relationships of the same form will be applicable to dilute solutions of long chain molecules; therefore, for small $v_1$'s and $v_2$'s the heat of dilution may be expressed by

$$\Delta \bar{H}_1 = \alpha_1 v_2^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

$$\Delta \bar{H}_2 = \alpha_2 v_1^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

Combination of equations (23) and (24) with the entropy equations (17) and (18a) give complete expressions for the free energies of the polymer/liquid system. The expressions for free energies of dilution and solution will not be exact, since equations (23) and (24) are only approximations, but will be of the form

$$\frac{\Delta \bar{S}_1}{v_2^2} + \frac{\Delta \bar{G}_1}{T v_2^2} = \frac{\alpha_1}{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

$$\frac{\Delta \bar{S}_2}{v_1^2} + \frac{\Delta \bar{G}_2}{T v_1^2} = \frac{\alpha_2}{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

Introducing the theoretical expression for $\Delta \bar{S}_1$ from equation (17)

$$\Delta \bar{G}_1 = RT[\ln(1 - v_2) - \left(1 - \frac{1}{n}\right) \frac{z'}{2} \ln(1 - 2v_2/z')] + \alpha_1 v_2^2 \quad (27)$$

and on expanding the second logarithm in series and ignoring terms beyond the second, the equation simplifies to

$$\Delta \bar{G}_1 = RT[\ln(1 - v_2) + \left(1 - \frac{1}{n}\right) . v_2 + \mu v_2^2] \quad . \quad (28)$$

where $$\mu = \frac{1}{z'} + \frac{\alpha_1}{RT} \text{ (when } n \text{ is large)} \quad . \quad . \quad . \quad . \quad . \quad (28a)$$

The corresponding equation for $\Delta \bar{G}_2$ may be shown to be

$$\Delta \bar{G}_2 = RT[\ln v_2 + (1 - n)v_1 + n\mu v_1^2] \quad . \quad . \quad . \quad (29)$$

HUGGINS [8] has shown that the somewhat limited published data on solutions of high polymers agree very well with equation (28). In accordance with theory, $\mu$ is found to be characteristic for a given solvent/polymer pair at a given temperature and apparently independent of concentration. Thus, rearranging equation (28), substituting $\ln(1 - v_2) = \ln v_1$ and $\Delta\bar{G}_1 = RT \ln a_1$, where $a_1$ is the thermodynamic activity of the solute in the solvent, it follows that

$$\frac{\ln a_1 - \ln v_1}{v_2} - 1 = -\frac{1}{n} + \mu v_2 \quad . \quad . \quad . \quad (30)$$

The plot of the left hand member of this equation against $v_2$ should give a straight line (if $\mu$ is constant) having a slope equal to $\mu$ and an intercept equal to $-\frac{1}{n}$. The experimental data for the rubber/benzene system, plotted in *Figure 22*, shows that $\mu$ has the constant value 0·43 over the whole range of composition within the experimental error. The enormous departures of this system from ideality are shown in *Figure 23*. These curves show a comparison of the activity, calculated from equation (30), plotted against the mol fraction of rubber $N_2$ (in benzene), for molecular weights of 1,000 and 300,000, with $\mu = 0{\cdot}43$ together with the activity value required if Raoult's law holds over the entire concentration range.

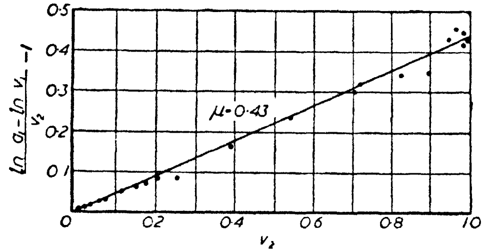

*Figure 22. Determination of $\mu$ for rubber/benzene system at 25° C from data of Gee and Treloar (Reference : 4d)*

From equation (28), on expanding the logarithm and putting $n = \frac{\bar{V}_2}{\bar{V}_1}$ (ratio of the partial molal volume of polymer to solvent molecule) it follows that

$$-\Delta G_1 = RT\frac{\bar{V}_1}{\bar{V}_2} \, . \, v_2 + RT(\tfrac{1}{2} - \mu)v_2^2 + RT\frac{v_2^3}{3}$$
$$+ \text{ higher terms in } v_2 \quad . \quad (31)$$

For dilute solutions the value of the third term is small and the higher terms in $v_2$ may be neglected. The value of the first term is determined principally by the molecular weight of the polymer $\left(n = \frac{\bar{V}_2}{\bar{V}_1}\right)$, and thus, except for the effect of molecular weight, the quantity $\mu$ dictates the value of $\Delta\bar{G}_1$. For example, if $\Delta\bar{G}_1$ is negative, the polymer will be soluble, and this is determined by the value of $\mu$. It is obvious that $\mu$ is an important quantity in the theory of polymer solutions, and its properties must be examined more closely.

The magnitude of $\mu$ depends on several factors, the most important of which, by definition, equation (28*a*), is the heat of mixing. Even in the absence of a heat of mixing, $\mu$ will have a finite value related to $z'$, and thus to the shape of the molecule. Huggins [8] has shown that $\mu$ is dependent only to a slight extent on the flexibility of the molecular chains. Both the heat of mixing contribution to $\mu$ and the contribution to $\mu$ of the entropy of mixing resulting from departures from perfect mixing would be expected to be smaller at higher temperatures. From equation (28*a*) it is seen that the temperature dependence of $\mu$ may be generally formulated by the equation

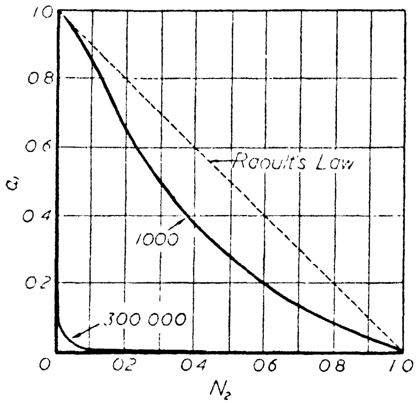

*Figure 23. Activity as a function of mol fraction for rubber/benzene system* $\mu = 0{\cdot}43$ *and molecular weights* = 1000 *and* 300,000

(*Reference : 4d*)

$$\mu = \beta + \frac{\alpha_1}{RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

where $\beta$ is an empirical constant and $\alpha_1$ is the contribution of the heat of dilution $\Delta \overline{H}_1$, which like $\beta$ varies with composition.

For the system rubber/benzene, $\mu$ was found to be independent of concentration. Unfortunately, in no other case has this concentration dependence of $\mu$ been examined over a sufficiently wide range, and although in most cases for dilute solutions $\mu$ seems to be independent of concentration for a given solute/solvent system, it cannot be taken for granted that that conclusion is generally valid.

In spite of the success of the theoretical interpretation of $\mu$ and its dependence on various factors, agreement with experiment is attained by assigning to $\mu$ an arbitrary value which does not agree with theory. It is necessary that the value of $\mu$ should be determined experimentally for a given solvent/solute combination. This requires the evaluation of a colligative property of the binary mixture such as vapour pressure or osmotic pressure, which can be related to the change in free energy by the fundamental expressions (1) or (4).

## PRESENT POSITION OF THEORY

Only in the case of rubber in benzene have separate evaluations of the partial molal free energy, entropy and the partial molal heat of dilution been made. The general conclusions from these studies, which are generally supported by the fragmentary evidence with other polymer solutions, are that the partial molal entropy is not entirely in accord with equations (18) or (19) for dilute solution, and neither is the heat of dilution consistent with the expression (23) over the whole concentration range. Yet a combination of these two functions leads to a free energy function which represents correctly the isothermal dependence of free energy on composition in polymer/solvent systems, the heat of mixing of which is small, when $\mu$ is treated as an empirical constant. The limitation of theory in accounting for entropies in dilute solution is offset on combination with the empirical $\mu$ term, since the latter includes not only the heat term, but also contributions from other factors, the origin of which is not clear. Thus, GEE[9] has recently shown that the non-dependence of $\mu$ on concentration arises from an approximate cancellation of the concentration dependence of $\alpha$ and $\beta$ in the $\mu$ equation.

In the present theory of polymer/solvent systems the entropy has been calculated assuming random mixing. The occurrence of a positive heat of mixing implies a non-random mixing, and attempts to include interaction energies in enumerating the configuration of the polymer molecule in terms of the lattice model have been made by GUGGENHEIM[10] and ORR.[10a] The resulting changes in the theoretical magnitude of $\Delta\bar{S}_1$ are, however, small, even for large heats of dilution.

In spite of this somewhat paradoxical situation, the success of the semi-empirical free energy expression justifies considerable confidence being placed in its application to the colligative and other properties of polymer solutions. This optimism is borne out by the usefulness of the $\mu$ function in discussing the special problems of solubility, swelling, *etc*, described in the following sections.

# II

# THE APPLICATION OF THERMODYNAMICS TO SPECIFIC PROBLEMS

## SOLUBILITY

The process of the interaction of long chain molecules with low molecular weight solvents, which includes solubility, swelling and plasticization, is of great importance both to research and to industry. These closely related properties are distinguishable in the sense that they differentiate the degree of separation of the molecules of polymer. Solution at one extreme consists of complete separation of the molecules, whilst during swelling the polymer absorbs solvent, yet the separation of molecules is not complete and the solid polymer maintains a well defined structure. In the very concentrated solutions of polymers containing 60 per cent or more of polymer, which are familiar as many commercial plastics, the low molecular weight component is usually referred to as a plasticizer, rather than a solvent. These concentrated mixtures have the characteristic property of high rigidity at ordinary temperatures, and their ‘ softness ’ depends on the relative amount of solvent content.

The nature of the various types of phase equilibria between simple liquids, and between liquids and crystalline solids, has been extensively studied, and the general principles governing these equilibria satisfactorily established. The new features introduced when these generalizations are extended to large molecules are a result of the size and flexibility of the molecules. A high molecular weight amorphous polymer, such as rubber or polystyrene, when immersed in a solvent (benzene) does not pass into solution immediately, but at first increases in volume, owing to imbibition of solvent; then, after a time, dispersion slowly occurs to form a true solution. If the liquid is a poor solvent, dissolution does not occur and the polymer swells to a more or less equilibrium size. In a good solvent, and with fairly low molecular weight polymers, dispersion may occur without preliminary swelling.

In considering the phase equilibria, the structure of the solid must be taken into account. Polymers exhibit a complete range of states from the highly crystalline to the purely amorphous form. The distinctions are not sharp and are largely determined by the nature of the forces between, and by the stereochemistry of the chains. These factors will influence the solubility in the sense that attraction between the chains opposes the tendency of the molecules to pass into solution. Energy considerations are not, however, the most important factors, since the solubility is determined by the free energy change of the separation of solute particles from their neighbours and of solvent molecules from other solvent molecules, and by the free energy gained when solute molecules interact with solvent molecules. The net free energy change will thus be dependent on both the structure of the solid and the nature of the solvent, and will be determined by the heat and entropy changes in the solution process. As may be anticipated from the theoretical considerations of the previous section, the high solubility of long chain molecules is a consequence of the high entropy of solution.

The various types of phase equilibria encountered in polymer systems can be demonstrated by considering the border or solubility curves of a polyethylene in a number of liquids of varying solvent power.[11] These are shown in *Figure 24*. The curves exhibit two main features: *a* the approximately linear portions *AB*, *AB′*, *AB″* at high polyethylene concentrations represent the depression of the melting point of the polymer by the solvents. On cooling a single phase mixture in this concentration range, a crystalline solid phase separates; *b* the prominent loop, concave to the composition axis, with a peak at low polyethylene concentrations. The liquid loop is not shown by ‘ good ’ solvents, such as xylene, and the solubility curve now represents the depression of the melting point of the polyethylene crystallites by the solvent.

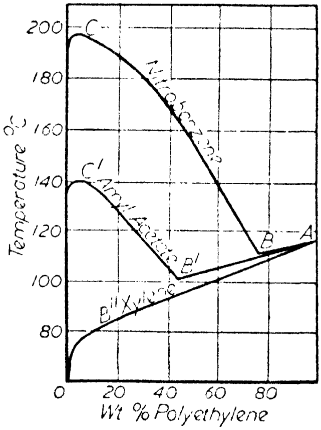

*Figure 24. Solubility curves for polyethylene in nitrobenzene, amyl acetate, xylene*
(*Reference* : 11)

The solubility curves of *Figure 24* represent the temperatures at which there is a change from a single liquid phase into a two-phase system. At lower temperatures a third phase may appear. Thus, on cooling a mixture rich in polythene, a temperature is reached at which a second liquid phase is formed, consisting predominantly of solvent. This equilibrium is between solid polyethylene and solvent, and is also the swelling equilibrium which can be studied by soaking polyethylene sheet in excess solvent and measuring the amount of liquid absorbed by the polyethylene. The curve showing this equilibrium in *Figure 24* may be regarded as an extension of the sections of the curves *CB*, *C'B'*, and represents the composition of the polyethylene-rich phase about to form a second solvent-rich liquid phase.

When a dilute solution of polyethylene is cooled to temperatures below the border curve, the longer molecules are concentrated in the precipitated phase. As the temperature is further reduced, the concentration and average molecular weight of polyethylene in solution are reduced. *Table XVII* shows the results obtained on cooling a 2·25 per cent solution in xylene. The last column gives the solubility of the same polyethylene at the temperature in question—that is, the maximum concentration of polyethylene in the single phase system.

*Table XVII*

*Distribution of Polyethylene between Precipitate and Filtrate from a 2·25 per cent Solution in Xylene*

*(Original molecular weight = 13,900)*[11]

| *Temperature °C* | *Wt fraction of polymer in the filtrate* | *Mol wt of polyethylene in filtrate* | *Concn of filtrate, wt % of polymer* | *Solubility of polymer in single phase (wt %)* |
|---|---|---|---|---|
| 20 | 0·007 | 1,200 | 0·016 | <0·001 |
| 51 | 0·034 | 3,800 | 0·076 | 0·006 |
| 54 | 0·047 | 4,800 | 0·167 | 0·012 |
| 58 | 0·094 | 7,700 | 0·220 | 0·035 |
| 62 | 0·254 | 13,000 | 0·571 | 0·100 |
| 65 | 1·000 | 13,900 | 2·250 | 2·250 |

This illustration, although it does not represent the complete phase equilibria, which, even in this simple system, are very complex, brings out very clearly the essential feature of the solubility phenomena, such as precipitation and fractionation, critical solution and swelling equilibria. These properties may now be examined in a more general and quantitative manner.

## SEPARATION OF PHASES: GELS

The application of equations (28) and (29), p. 124, for $\Delta\overline{G}_1$ and $\Delta\overline{G}_2$ allow the calculation of solubility conditions and the distribution of polymer between two phases.[13] If $\Delta\overline{G}_1$ or $a_1$ is plotted against decreasing $v_1$, it is found that at sufficiently small values of $\mu$, $\Delta\overline{G}_1$ decreases uniformly, signifying complete miscibility of solvent and polymer (*Figure 25*); with larger values of $\mu$ (*i.e.*, large heats of mixing), however, the curves show a minimum and a maximum, indicating a separation of the system into two phases. There will therefore be a critical value of $\mu$, denoted by $\mu_{crit}$, at which the solution breaks into two phases. For this value the curve will show a point of inflection, and applying the usual condition that here the first and second derivatives of $\Delta\bar{G}_1$ with respect to $v_2$ must vanish, it follows that

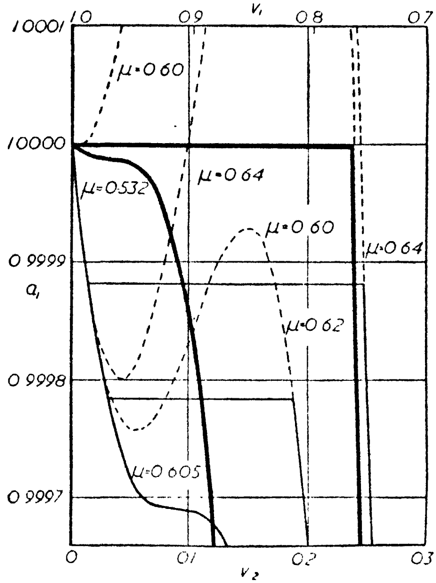

*Figure 25. Activity* ($a_1$) *versus volume fraction for* $\bar{V}_2/\bar{V}_1 = 100$ (*lighter lines*) *and* 1,000 (*heavier lines*) *at different values of* $\mu$
(*Reference* : 4*b*)

$$\mu_{crit} = \frac{1}{2}\left[1 + \left(\frac{1}{m/m_0}\right)^{\frac{1}{2}}\right]^2 = \frac{1}{2}\left[1 + \left(\frac{\bar{V}_1}{\bar{V}_2}\right)^{\frac{1}{2}}\right]^2 \quad . \quad (33)$$

where $m$ is the molecular weight of polymer, assumed for the present to be homogeneous, and $m_0$ is the molecular weight of the monomer unit. If one component has a high molecular weight with respect to the other component, the critical value of $\mu$ is very close to one half. This critical point[3] corresponds to critical values of

$$(v_1)_{crit} = \frac{1}{1 + \frac{1}{\sqrt{m/m_0}}} \quad . \quad . \quad . \quad . \quad . \quad (34)$$

$$(v_2)_{crit} = \frac{1}{1 + \sqrt{m/m_0}} \quad . \quad . \quad . \quad . \quad . \quad (35)$$

The shapes of the curves of *Figure 25* shows that in the region of partial miscibility, the solvent is much more soluble in the polymer than the polymer in the solvent; in fact, one phase (the supernatant liquid) is almost pure solvent (if $\frac{\bar{V}_2}{\bar{V}_1} = 1{,}000$, $v_1 \geq 0{\cdot}97$, $a_1 \simeq 1$) while the precipitated phase is a swollen polymer. This is in agreement with the findings of BRÖNSTED and VOLQUARTZ [13] on the swelling of polystyrene in laurate esters and those of GEE [14] on rubber in various solvents. The concentration in the polymer-rich fraction is so high that the mutual interference of chains occurs and they adhere on contact, so that the solution will show a degree of rigidity, and it will have the properties of a gel. The same theoretical treatment has been extended by HUGGINS [12] to the solubility of small molecules in gels.

## SOLUBILITY RELATIONSHIPS

The solubility at any other point than the critical may be determined by use of the condition for equilibrium between the two phases—namely, that the partial molal free energy of each constituent is the same in both phases. Using primes to signify the swollen polymer phase, the condition may be expressed

$$\Delta\bar{G}_1 = \Delta\bar{G}_1' \quad \text{and} \quad \Delta\bar{G}_2 = \Delta\bar{G}_2'$$

Substituting from the free energy equation (28), then for a homogeneous polymer

$$\begin{aligned} \ln v_1 + 1 - v_1 - \frac{1 - v_1}{n} + \mu(1 - v_1)^2 \\ = \ln v'_1 + 1 - v'_1 - \frac{1 - v'_1}{n} + \mu(1 - v'_1)^2 \quad (36) \end{aligned}$$

$$\begin{aligned} \ln v_2 + (1 - n)v_1 + n \,.\, \mu v_1^2 \\ = \ln v'_2 + (1 - n)v'_1 + n \,.\, \mu v'^2_1 \quad . \quad . \quad . \quad (37) \end{aligned}$$

Solving equations (36) and (37) for $\ln \frac{v_1}{v'_1}$ and $\ln \frac{v'_2}{v'_1}$, and comparing, one obtains

$$\ln \frac{v'_2}{v_2} = n\left\{2\mu(v_1 - v'_1) - \ln \frac{v_1}{v'_1}\right\} \quad . \quad . \quad . \quad (38)$$

For the dilute solution phase, $v_1 \simeq 1$. Experimental evidence indicates that the composition of the second phase is almost independent of molecular weight, and thus $v'_1$ may be treated as a constant. Equation (38) thus takes the form

$$\ln \frac{v'_2}{v_2} = nA \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (39)$$

where $A = 2\mu(v_1 - v'_1) - \ln v_1/v'_1$, and is a constant for any system.

This equation is of the form used very much earlier by Brönsted, who derived equation (39) on the assumption that distribution of the molecules between the two phases was determined by energy differences

$$\ln \frac{c'}{c''} = \lambda m/RT \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (40)$$

where $c'$ and $c''$ are the concentrations of polymer in the two phases at equilibrium, $m$ is the molecular weight of the polymer and $\lambda$ is a constant characteristic of the polymer/solvent system but independent of $m$. He considered $\lambda$ to be continuously variable along a series of liquids and hence, as $\lambda$ decreased through zero and became negative, the distribution underwent a sudden change of character. With $\lambda$ negative, $\frac{c'}{c''}$ is small and the liquid is a non-solvent; with $\lambda$ positive, $\frac{c'}{c''}$ is large and the liquid is a perfect solvent. These predictions accounted very satisfactorily for the various types of equilibria encountered in polymer/solvent systems and were confirmed by Brönsted's own investigations with polystyrene. SCHULZ[15] extended this theory to mixed liquids by assuming that in a binary mixture $\lambda$ was a linear function of the composition. He deduced the equation

$$\gamma = A' + \frac{B'}{m} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (41)$$

which expresses the relation between $\gamma$, the critical composition which is just a solvent (*i.e.*, at the precipitation point) and $m$ the molecular weight, $A'$ and $B'$ being constants. This equation, like equation (40), has been widely used and satisfactorily represents the data for several high polymers. In spite of this success, the theory upon which these equations are based is incorrect, since, as has already been shown, the free energy changes are determined mainly by the entropy of mixing—a factor ignored in the Brönsted–Schulz theories—and not entirely by the heat term. Although the form of the equation seems correct, the true derivation is that given at the beginning of this paragraph which, besides providing a sound theoretical basis, also gives an interpretation of the constants.

## FRACTIONATION

Many of the important properties of high polymers depend on the distribution of molecular sizes in the heterogeneous material. Methods of determination of the distribution curve are thus of fundamental importance in the correlation of physical and mechanical properties with the property of heterogeneity of the polymer. Furthermore, the preparation of fractions, at least approaching homogeneity with respect to molecular weight, is a necessary preliminary procedure in the application of viscosity methods to the determination of molecular weights; it is also an invaluable procedure in the elucidation of the kinetics and mechanisms of polymeric reactions.

The most important and widely used methods of fractionation depend on the greater solubility, in a given solvent, of the low molecular weight species and on the fact that the solvent power of a mixture of liquids (solvent and non-solvent) depends on the proportion of the two liquid components. In general, two experimental procedures have been used: *1* Fractional precipitation, in which the polymer is completely dissolved in a suitable liquid and the non-solvent or precipitant is added. Proper adjustment of the relative amounts of solvent and precipitant gives a two-phase system at equilibrium—the ‘ precipitated ’ phase which contains the high molecular weight fraction and the supernatant liquid containing the lower molecular weight polymer in solution. The liquid is then separated by decantation, more polymer is precipitated, and the process repeated. There are two principal ways in which the precipitation can be effected: *a* by adding a precipitant isothermally; *b* by lowering the temperature, keeping the total composition constant. Both methods have been widely used. *2* Fractional solution, in which the polymer is placed in contact with a solvent/non-solvent mixture, and the system allowed to come to equilibrium. The supernatant liquid is decanted and the residue treated with a fresh mixture richer in solvent than the first and the process repeated until all the polymer has dissolved. In this way the low molecular weight fractions are extracted first. The whole subject has been reviewed recently.[16]

The theoretical results described so far were developed for a homogeneous polymer, and we now have to consider their application to mixtures of species of different molecular weights. In both methods (fractional precipitation and fractional solution) the separation into successive fractions depends on a controlled alteration of $\mu$ in the critical region for precipitation. As we have already demonstrated, the critical region corresponds to a $\mu$ value equal to one half. Fractionation gives two phases, each containing a portion of the polymer, the concentration in the precipitated phase being much greater than in the supernatant phase. The resulting fractions are not sharp; each fraction contains a wide range of species, although it is less heterogeneous than the original polymer. Equations (28) and (29) provide a means for calculating the degree of separation obtained under various conditions, and for clarifying the factor affecting the sharpness of separation.

These equations were derived for a homogeneous polymer. The corresponding relationships for heterogeneous polymers have been derived by GEE,[17] FLORY [18] and by SCOTT and MAGAT,[19] who showed that the partial molal free energy of the solvent and of an $x$ mer in a solution of a heterogeneous polymer is given by

$$\Delta\bar{G}_1 = RT\left[\ln(1 - v_2) + v_2\left(1 - \frac{1}{\bar{x}_n}\right) + \mu v_2^2\right] \quad . \quad (42)$$

$$\Delta\bar{G}_x = RT\left[\ln v_x + v_2 x\left(1 - \frac{1}{\bar{x}_n}\right) + \mu x(1 - v_2^2)\right] \quad . \quad (43)$$

where the volume fraction of all polymer molecules $= v_2 = \Sigma v_x$ and $\bar{x}_n$ is the number average molecular size. The equilibrium conditions between the two phases can now be expressed as previously by equation (44), *viz*

$$\Delta\bar{G}_1 = \Delta\bar{G}_1'; \ \Delta\bar{G}_x = \Delta\bar{G}_x' \quad . \quad . \quad . \quad . \quad (44)$$

where the primes refer to the precipitated phase. Substituting from the above equation, and evaluating $v_x'/v_x$, the expression obtained is

$$\ln v_x'/v_x = x \, . \, A \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (45)$$

where $A = v_2\left(1 - \frac{1}{\bar{x}_n}\right) - v'_2\left(1 - \frac{1}{\bar{x}'_n}\right) + \mu[(1 - v_2)^2 - (1 - v'_2)^2]$

This equation shows that the ratio of the concentration of a given species in the two phases varies exponentially as $x$. The application of this equation to fractionation has been discussed by Flory [18] and Gee,[17] and both authors reach the significant conclusion that the efficiency of separation depends on the ratio of the volumes of the supernatant and the precipitated phases. In order to attain a high value for this ratio, very dilute solutions may be employed, and the higher the molecular weight at which separation occurs the greater the dilution required for the same sharpness of separation. These theoretical conclusions are supported by experiment and have proved valuable guides in carrying out fractionation. Fractionation is never completely efficient; the fractions are never homogeneous with respect to molecular weight, although much more nearly so than the unfractionated material.

## SWELLING

When a high polymer is placed in contact with a suitable solvent, the polymer is observed to swell as the result of the imbibition of the solvent. This implies that the groups present in the polymer molecule interact energetically with solvent molecules and, in complete analogy with solubility studies, this interaction is most marked between related groups. Thus, hydrocarbon or chloride polymers swell in hydrocarbons or chlorinated solvents; polymers with pronounced hydrophilic structural units, OH, COOH, *etc*, swell readily in water or other hydrogen bond-forming solvents. If the polymer molecules consist essentially of linear chain structures of finite size, the swelling is limited only by the amount of solvent available; in a large amount of solvent the polymer will dissolve completely. If, however, the polymer consists of a cross linked or continuous network structure, as in the case of a vulcanized rubber, the amount of liquid absorbed will reach a limit beyond which no further swelling occurs, and a well defined swelling equilibrium state is established. The swelling may be regarded as the expansion of the network structure by the imbibed solvent up to the point where the elastic forces in the chains of the network counterbalance the tendency towards dilution by the solvent. The greater the number of cross links in the gel the less it will swell in contact with the liquid. In the case of a ‘ loose ’ gel structure possessing few cross links swelling may exceed a fiftyfold increase in volume; a strongly vulcanized or highly cross linked structure will swell only two- or threefold.

Limited swelling may be shown by a ‘ crystalline ’ chain polymer consisting of crystalline and amorphous regions. The solvent may readily penetrate into the amorphous regions, but does not disrupt the separate chains, which remain held together by the strong forces in the crystalline regions. It is usually possible to bring this class of polymer into solution by choice of a suitable swelling agent or by raising the temperature. Thus polythene swells in amyl acetate or nitrobenzene, but is completely soluble in xylene.

FRENKEL [20] and GEE [7] first proposed that the swelling for three-dimensional gel structures, by absorption of solvent, was due to osmotic forces. The consequent expansion of the network may be regarded as analogous to an elastic deformation. Equilibrium is attained when the osmotic pressure balances the elastic reaction of the network. Solvent in the gel is in equilibrium with excess solvent, and the equilibrium condition is that the partial molal free energy of the solvent in the gel shall equal the partial molal free energy of the unabsorbed solvent. For equilibrium with pure solvent, $\Delta\bar{G}_1 = 0$, where $\Delta\bar{G}_1 = \Delta\bar{G}_{m_1} + \Delta\bar{G}_{el}$. $\Delta\bar{G}_{m_1}$ is the osmotic and $\Delta\bar{G}_{el}$ the elastic contribution to the partial molal free energy; thus $\Delta\bar{G}_1$ may be written

$$\Delta\bar{G}_1 = \Delta\bar{H}_1 - T\Delta\bar{S}_{m_1} - T\Delta\bar{S}_{el} \quad . \quad . \quad . \quad . \quad (46)$$

The entropy term $\Delta\bar{S}_{m_1}$ arises from the mixing of the chains with solvent and $\Delta\bar{S}_{el}$, the entropy change due to expansion of the network.

FLORY and REHNER [21] extended the statistical mechanical theories previously developed for dilute polymer solutions to cross linked polymers and showed that

$$\Delta\bar{S}_{el} = -R\rho V_1 v_2^{1/3}/m_c \quad (47)$$

where $\rho$ = density of polymer; $V_1$ = molar volume of solvent; $v_2$ = volume fraction of polymer at swelling equilibrium; $m_c$ = average molecular weight between cross links.

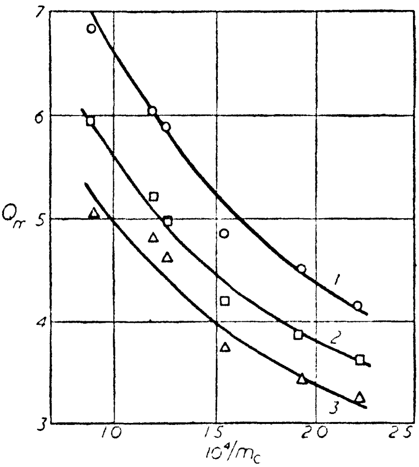

*Figure 26. Effect of cross linking of rubber on swelling capacity in good solvents*

1 *carbon tetrachloride*
2 *carbon disulphide*
3 *benzene*
(*Curves theoretical*)
(*Reference* : 9)

Hence
$$\begin{aligned}\Delta\bar{G}_1 &= RT[\ln(1 - v_2) + v_2 + \rho V_1 v_2^{1/3}/m_c] + \Delta\bar{H}_1 \quad (48)\\ &= RT[\ln(1 - v_2) + v_2 + \rho V_1 v_2^{1/3}/m_c + \mu v_2^2] \quad (49)\\ &= 0 \text{ at equilibrium.}\end{aligned}$$

Thus, from the experimental measurement of the extent of swelling, $m_c$, the molecular weight per chain, may be evaluated, or $\mu$, if $m_c$ is known.

Equation (48) has been tested from measurements of the swelling of butyl rubbers in *cyclo*hexane and of ordinary vulcanized rubber in a number of liquids differing widely in chemical type and in solvent power.[9, 22] The experimental measurement of the degree of swelling is very simple; weighed samples of the rubber (*ca* 1 g) are immersed in excess liquid and maintained at constant temperature for several days or until swelling is complete, then removed quickly, surface dried and weighed. The results for some good swelling agents are shown in *Figure 26*, in which the degree of swelling $Q_m$ (the equilibrium volume of solvent absorbed by 1 g of solid) is plotted as a function of $\frac{1}{m_c}$ for a series of natural rubber vulcanizates. ($m_c$ was determined from elastic tension measurements on the swollen rubber.)

For isotropic swelling, it follows from equation (49) since $Q_m = \frac{1}{v_2} - 1$, that the effect of $m_c$ is given by

$$\ln\left(1 + \frac{1}{Q_m}\right)^{-1} + (Q_m + 1)^{-1} + \mu(Q_m + 1)^{-2} = \frac{\rho V_1}{m_c} \cdot (Q_m + 1)^{-\frac{1}{3}} \qquad (50)$$

The theoretical curves drawn in *Figure 26* were calculated from this equation; using a value of $\mu$ selected to give the best representation of the points. The values of $\mu$ derived by Huggins from vapour pressure data (page 125) were in fairly good agreement with those from swelling data, showing that equation (50) is reasonably satisfactory.

## OSMOTIC PRESSURE

The osmotic pressure of dilute solutions of polymers may be deduced directly from equations (4) and (21) (pp. 118, 124). The relationships obtained find their main application in connection with molecular weight determinations. These are discussed in detail in Chapter 5 (page 156).

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## CHAPTER 5

# SIZE AND SHAPE OF MACROMOLECULES

## I

## SHAPE OF LINEAR MOLECULES IN SOLUTION

IN THE PREVIOUS chapter it was shown that the difference in behaviour and properties of macromolecules in solution from those of small molecules was a direct consequence of the size and configuration of the large molecules. Conversely, it is from the study of the properties of polymer solutions that our knowledge of the shape of the molecules is obtained. Before discussing the detailed methods of investigation and the results obtained, it may be useful to consider briefly the configuration and properties of a macromolecule in dilute solution. Our observations will be confined to linear chain structures because, at the present time, our knowledge of branched structures is extremely limited. As yet no satisfactory method of controlling or determining branching has been found, and the more complex three-dimensional structures are not amenable to investigation in solution.

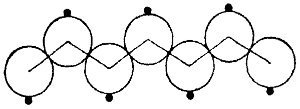

*Figure 27. Carbon skeleton of hydrocarbon chain (side groups are indicated by black dots)*

Taking a long chain of $CH_2$ groups as the simplest type of structure, both from the geometric and chemical points of view, the segments connecting each carbon atom will make with each other an angle of 109°, characteristic of the tetrahedral valencies of the carbon atom. The configuration of such a chain in the crystalline solid state can be schematically represented by the carbon skeleton of the chain, as shown in *Figure 27.* In dilute solutions, when the individual molecules are isolated, many other conformations of the molecule are possible, as a result of free rotation about the C—C single bond. If there were no interfering effects, all configurations differing by rotation of one part of the chain with respect to the other about any single bond would be possible, since all these forms would have the same potential energy. This conclusion would be equally true for any single bond of the type C—O, C—N, C—S, *etc*, which can be rotated freely about its axis, but it is no longer valid with complex molecules in which all the valencies of the carbon atoms are saturated by attachment of other atoms or groups. If the chain is now imagined to be rotated with the preservation of the valency angles, the side groups will become closer together and, in general, free rotation will be resisted by mutual repulsion of the side groups. Experimental evidence shows that even with the small hydrogen atom attached to the carbon in the $CH_2$ chain, free rotation around the carbon–carbon bond requires an activation energy of 3,000 cal per mol. On the other hand, free rotation around multiple bonds such as C=C, C≡C, C≡N, *etc* is inhibited altogether, but the presence of such groups in the chain molecule has a beneficial effect on the rotation of adjacent groups. Thus, in $—CH_2—C≡C—CH_2—$ the energy of rotation around the $C—CH_2$ bond is lowered to about 500 cal/mol, owing to the absence of $CH_2—CH_2$ interactions. The presence of linkings such as C—O—C, —C=N—, *etc*, would have a similar influence on the freedom of rotation.

Linear molecules, by twisting or rotating about single bonds, can therefore take up an enormous number of configurations of approximately the same energy. Given the direction of the first bond, the second may be restricted by potential energy effects to certain definite directions, but bonds a little farther down the chain will take up positions quite independent of the fixed orientation of the first. Flexibility of the chain system may therefore be regarded either as a complete rotation about single bonds, or as a system of rigid links which can take up orientations independently of adjacent links. Each configuration of the chain will correspond to a definite distance $r$ between its ends, which will be called the displacement length of the chain. The same value of $r$, of course, may be attained from a large number of different configurations. From the point of view of the theory of free rotation, all these configurations are equally probable, and the probability $W(r)dr$ that the effective length lies between $r$ and $r + \delta r$ is therefore proportional to the number of configurations. It is obvious that the probability of the maximum value of $r$, which corresponds to the fully extended chain, is vanishingly small and that the highly contorted forms are the most probable. GUTH, MARK and KUHN,[1] from theoretical studies, have concluded that the probability of a length between $r$ and $r + \delta r$ for the vector connecting the ends of a chain, which is free to assume irregular configurations at random, is given by

$$W(r)dr = (4\beta^3/\pi^{\frac{1}{2}}) \exp(-\beta^2 r^2) r^2 dr \quad . \quad . \quad . \quad (1)$$

where $\beta$ is a parameter, the value of which will depend on the length of the chain and its flexibility.

The relative numbers of chains of various lengths $r$ are shown graphically in *Figure 28*. The most probable length $r_{max}$, the average, and the root mean square lengths are given by

$$r_{max} = \frac{1}{\beta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$\bar{r} = \sqrt{\frac{4}{\pi}}\,\beta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$\sqrt{\bar{r^2}} = \sqrt{\frac{3}{2}}\,\beta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

For a chain of $Z$ bonds, each of length $l$, EYRING[2] has shown that, assuming free rotation about each bond and tetrahedral angles between successive bonds, then

$$\bar{r^2} = 2l^2Z$$

and hence for free rotation

$$\beta = \sqrt{3/4Zl^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Substituting (5) in (1) gives an expression for the probability of distribution of chain displacement length $r$ as a function of the chain contour length $Z \,.\, l$.

In general, steric effects in the long polymer molecules will hinder the free rotation about the single bonds, and detailed analysis has shown that this increases the mean displacement length of the chain over that which prevails for free rotation. Even in these instances, the mean displacement for long chains will usually remain only a fraction of the chain contour length, and very rarely will the fully extended length be expected.

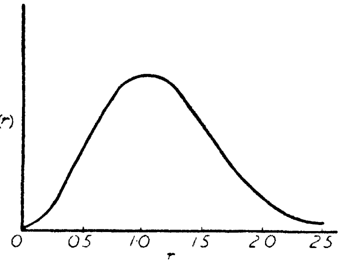

*Figure 28. Theoretical distribution of distances r between the ends of long randomly kinked chains where r is expressed in terms of $r_{max}$ (see equations 1 and 5)*

The expansion of the configuration with increasing hindrance to free rotation will be important in determining the form taken up by the molecules in solution, and should exert a noticeable effect on the properties of solutions of the polymer. For example, the more extended configuration will show higher viscosities in solution for the same contour length.

The degree of flexibility of the macromolecules will therefore depend on the backbone structure of the chain, and on the nature and size of the constituents distributed along its length. It is primarily these structural properties which confer on macromolecules their peculiar physical, mechanical and solution properties, and which determine their technical applications. For example, cellulose and its derivatives are characterized by relatively stiff main chains, whereas rubbers have chains with much more flexible backbones. The effect of this flexibility is to produce an irregular coiling and uncoiling of the molecule which, as we shall see, accounts for the elastic properties of this class of molecule. In view of this ' internal ' Brownian motion, together with the influence of the normal external Brownian movement of the solvent molecules, the shape of the molecule in solution is continually changing, and one can therefore speak only of the instantaneous shape of the molecule at a given moment. Hence it is preferable to refer to the average shape of the molecule, which is hypothetically obtained by averaging the various instantaneous configurations which would occur if the molecule could be observed over a long period of time. A wide variety of shapes is possible, depending on the flexibility of the chain, its interaction with the solvent, and on the temperature. Although we are justified in speaking of the size and shape of a polymer molecule, it should be realized that the terms refer to rather ill defined quantities.

Typical polymer molecules of high molecular weight, when fully elongated, may extend to several hundred Angström units in length, whereas the diameter is only a few Å. In the course of the internal and external Brownian movements such molecules require a relatively large volume, and contact and interaction of segments with other molecules, or even entanglement of the chains, may be frequent. Polymer aggregation of this type may easily falsify size determinations, and in carrying out such measurements it is necessary to work at as low a concentration as possible, and sometimes at elevated temperatures, in order to reduce interaction and agglomeration. The choice of solvent for measurement is important, since the average shape of the macromolecule will vary according as there is attraction or repulsion between polymer and solvent; furthermore, in the former case ' solvation ' will lead with some methods of determination to high molecular weights.

These introductory remarks serve to emphasize the need for caution in attempting to specify precisely the shape and size of macromolecules in solution. These magnitudes are very much dependent on the experimental conditions employed in their determination, and these should always be specified. We can now proceed to describe the experimental methods which have been employed in determining macromolecular dimensions.

## II

## MOLECULAR WEIGHT AVERAGES

Since all synthetic polymers and most of those available from natural products, are mixtures of macromolecules of different sizes, the molecular weights determined by various methods are averages. Different experimental methods do not always give the same average molecular weight. If we use a method which actually counts the number of molecules, for example, methods based on colligative properties such as osmotic pressure or freezing point lowering, or the determination of the end groups by chemical or physical methods, then the weight of polymer divided by the number of molecules gives the so-called number average molecular weight.

The number average molecular weight is represented by the symbol $\overline{m}_n$ and may be defined generally according to

$$\overline{m}_n = \frac{\sum\limits_i n_i m_i}{\sum\limits_i n_i} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where $n_i$ is the number and $m_i$ the molecular weight of the $i$th species.

On the other hand, light scattering and certain types of sedimentation measurements, in which the characteristic being measured depends not only on the concentration but also on the weight of the particle, give a weight average molecular weight ${}_w$ which is defined by

$$\overline{m}_w = \frac{\sum\limits_i n_i m_i^2}{\sum\limits_i n_i m_i} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

In the case of a mixture of small and large molecules, it follows that a small percentage (by weight) of the small molecules will have a large effect on lowering the number average molecular weight, whilst in weight average molecular determinations the fraction of highest molecular weight material has the more important effect.

A simple numerical example will illustrate these differences. For a mixture of equal numbers of molecules of weights 1,000 and 10,000, the number average molecular weight would equal 5,500, in spite of the fact that the molecules of the lower molecular weight contribute only $\frac{1,000}{11,000} = 9{\cdot}1$ per cent by weight to the mixture. The weight average molecular weight would equal 9,182, and could thus be more representative of the mixture. If the system consists of only one type of molecule, then $\overline{m}_n = \overline{m}_w$; otherwise $\overline{m}_w > \overline{m}_n$.

Viscosity measurements give either a weight average molecular weight or a more complex average defined by FLORY[3] as the viscosity average molecular weight, $\overline{m}_v$, depending on the observed experimental viscosity law. This will be discussed on page 177, where it will be shown that

$$\overline{m}_v = \left[\frac{\sum_i n_1 \overline{m}_i^{\beta+1}}{\sum_i n_1 \overline{m}_i}\right]^{1/\beta} \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where $\beta$ = constant. When $\beta = 1$, $\overline{m}_v$ becomes equal to $\overline{m}_w$. Other types of average are obtained by sedimentation equilibrium and sedimentation velocity measurements. The kind of average then obtained depends on the method of evaluation of the experimental measurements (page 151 *et seq*).

## III

## MOLECULAR WEIGHT DETERMINATION

### LIGHT SCATTERING MEASUREMENTS

In 1944 DEBYE[4] showed that when an unpolarized light beam was passed through a polymer solution, the intensity of the scattered light (turbidity) was closely connected with the molecular size and shape of the dissolved macromolecules. The method has rapidly become one of the most important tools in the study of high polymers in solution. The fundamental concepts of this method are soundly established, and will be briefly reviewed before we consider the application to specific problems.

It has been known for a long time that when a light beam passes through a non-absorbing liquid some light is scattered. This is a result of non-uniformities in the density of the liquid. If the solvent is made more inhomogeneous by the addition of solute molecules, the intensity of the scattered light is increased, and a measurement of this increase can be used to count the number of solute particles; furthermore, conclusions regarding the configuration of the particles can be drawn from observations of the angular distribution of the scattered light. The additional light scattered by dissolved particles was attributed by VON SMOLUCHOWSKI (1908) and EINSTEIN (1910) to non-uniformities arising from minute fluctuations in density and concentration which occur in any real solution. The extent of the fluctuations is determined by the work (free energy change) necessary to produce them, and on this basis the following expression for the turbidity of a colourless binary mixture was derived

$$\tau_0 = \frac{32\pi^3\mu_0^2}{3\lambda^4 N_0}\left\{RT\beta\rho\left(\frac{\delta\mu}{\delta\rho}\right)^2 + \frac{m_1 c}{\rho\left(-\frac{\delta \ln f_1}{\delta c}\right)}\cdot\left(\frac{\delta\mu}{\delta c}\right)^2\right\} \quad . \quad (9)$$

$\tau_0$ = turbidity of solution (corresponding to extinction coefficient in Lambert's Law); *i.e.* fractional decrease in intensity of light in traversing *one cm* of the solution, the decrease occurring by scattering and not by absorption
$\lambda$ = wavelength in vacuum
$N_0$ = Avogadro's number
$R$ = molar gas constant
$T$ = temperature (°K)
$\beta$ = isothermal compressibility of solvent
$\rho$ = density
$\mu_0$ = refractive index of solvent
$\mu$ = refractive index of solution
$m_1$ = molecular weight of solvent
$f_1$ = fugacity of solvent
$c$ = concentration of solute in g per [illegible] of solution

The first term represents the turbidity arising from fluctuations in density and corresponds essentially to the turbidity of the solvent (assuming $\beta$ = constant). Thus, if the measured turbidity of the solvent is subtracted from $\tau_0$, the remainder $\tau$ represents the turbidity caused by concentration fluctuation, a quantity which can be related directly to the molecular weight of the solute molecules. Thus, substituting the thermodynamic relation

$$-\frac{\delta \ln f_1}{\delta c} = \frac{\bar{V}_1}{RT}\left(\frac{\delta\Pi}{\delta c}\right)$$

where $\Pi$ = osmotic pressure and $\bar{V}_1$ = partial molal volume of solvent, which is approximately equivalent to $\frac{m_1}{\rho}$ for dilute solutions, it follows that

$$\tau = \frac{32\pi^3 c\mu_0^2(\delta\mu/\delta c)^2}{3\lambda^4 N_0 . 1/RT . \left(\frac{\delta\Pi}{\delta c}\right)} \quad . \quad . \quad . \quad . \quad (10)$$

The osmotic pressure/molecular weight relationship wherein $m_2$ = molecular weight of solute

$$\Pi = \frac{RT}{m_2} c + Bc^2 + \ldots$$

is soundly established for polymer solutions, equation (22) page 158, and thus $\frac{\delta\Pi}{\delta c}$ can be evaluated. In most cases it is found that $\mu - \mu_0$ is accurately proportional to the concentration within the range generally used for polymer solutions, and so $\delta\mu/\delta c$ may be replaced by $\mu - \mu_0/c$.

Hence $$H \,.\, c/\tau = \frac{1}{RT}\left(\frac{\delta\Pi}{\delta c}\right)$$

where $$H = \frac{32\pi^3}{3} \cdot \frac{\mu_0{}^2}{N_0\lambda^4} \cdot \left(\frac{\mu - \mu_0}{c}\right)^2$$

and therefore, substituting for $\delta\Pi/\delta c$, to a good approximation

$$H \,.\, c/\tau = \frac{1}{m_2} + 2Bc + \ldots \quad . \quad . \quad . \quad . \quad . \qquad (11)$$

The plotting of $H \,.\, c/\tau$ against $c$ gives a straight line which cuts the vertical axis at an ordinate which is equal to the reciprocal of the molecular weight of the solute, whereas the slope should be related to that obtained from the dependence of osmotic pressure on concentration. It can be shown that the measured molecular weight is a weight average molecular weight.[5]

In the practical applications of this method to molecular weight determinations, the only experimental measurements which are necessary for the calculation of $H \,.\, c/\tau$ are *a* the turbidity $\tau$ at a series of concentrations and *b* the dependence of refractive index on concentration. Since the fraction of light scattered is small, it is difficult to determine accurately the loss of intensity of a light beam passing through the solution contained in a cell, and so the intensity scattered by the solution at some angle, usually 90°, off the beam is measured. Some form of turbidimeter is used for this purpose. In determining $H \,.\, c/\tau$ it is usually sufficient to make one measurement of the difference between the refractive index of the solution $\mu$ and the solvent $\mu_0$, since $\mu - \mu_0$ is very accurately proportional to $c$. Since this difference is usually of the order of 0·001 for a 1 per cent solution, it is necessary to measure the difference to the fifth decimal place in order to obtain a 1 per cent accuracy in $\mu - \mu_0/c$. A differential refractometer containing a hollow prism has been developed by P. Debye [6] for this measurement. *Figure 29* shows the results of light scattering measurements for three polystyrene fractions in the same solvent.[7] The lines have different intercepts, but about the same slope. The molecular weight obtained from the intercept of *fraction 1* agreed very closely with the osmotic molecular weight determined for the same sample. The corresponding data for polystyrene in a mixed solvent,[8] benzene/methanol, the benzene being a good solvent and the methanol a poor solvent (precipitant), are shown graphically in *Figure 30*. The value of $H\,.\,c/\tau$ is plotted against $c$ for a given polystyrene fraction in different solvent mixtures. It will be observed that the straight lines have different intercepts, which indicates that the molecular weight increases with increasing non-solvent content. This effect has been shown to be due to the preferential adsorption of the benzene on the polymer particles, and this interpretation furnishes a quantitative measure of such preference.

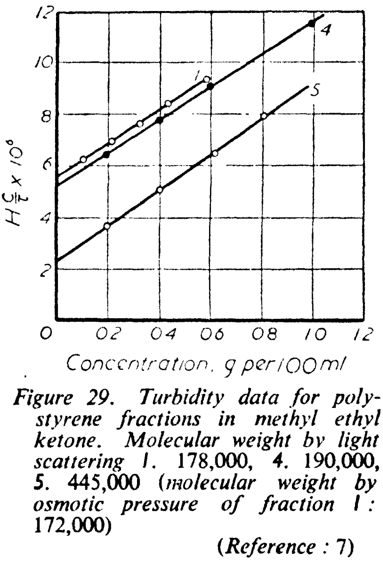

*Figure 29. Turbidity data for polystyrene fractions in methyl ethyl ketone. Molecular weight by light scattering 1.* 178,000, *4.* 190,000, *5.* 445,000 (*molecular weight by osmotic pressure of fraction 1 :* 172,000)

(*Reference :* 7)

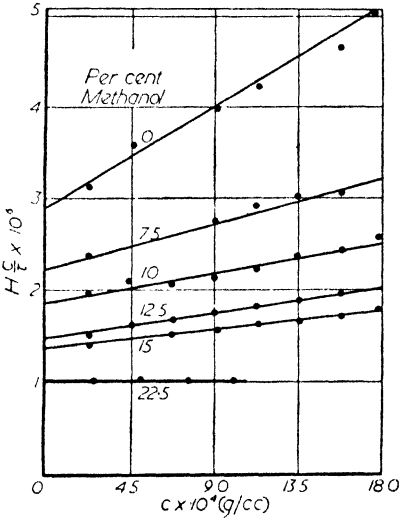

*Figure 30. Reciprocal specific turbidity of polystyrene in benzene/methanol mixtures*

(*Reference :* 8)

*Scattering by Large Particles*—The foregoing theoretical treatment is based on the assumption that the dimensions of the solute particles are small, compared with the wavelength of scattered light, and that every particle may be considered as a point source of radiation. When the largest dimension of the solute particle is less than one twentieth of $\lambda$, the scattered intensity does not depend on the angle at which it is observed. However, as soon as the largest dimension of the scattering particle becomes about $\frac{1}{20} . \lambda$ or larger, the scattering from different parts of the particle must be considered separately. The light scattered from different parts of the molecule differs in phase, owing to a difference in path length, and a greater path difference is produced in the backward than in the forward direction. This process will result in an interference effect, and a consequent all round decrease in scattered intensity, with a greater reduction in the backward direction.

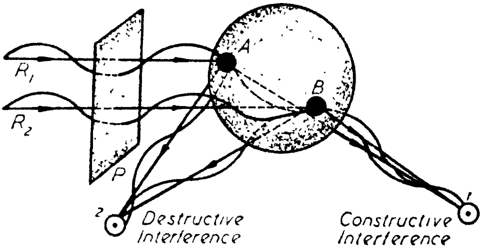

*Figure 31. Scattering from a large particle (Reference : 9)*

This phenomenon may be illustrated with the aid of a simple example.[9] The sphere in *Figure 31* represents a scattering particle the dimensions of which are of the order of magnitude of the wavelength. Consider two scattering volume elements of the particle at $A$ and $B$ and two incident rays $R_1$ and $R_2$ which are in phase at the plane $P$. In reaching the observation point $I$, ray $R_1$, which travels the shorter distance to reach element $A$, travels the longer distance $AI$; while the ray $R_2$, which travels the longer distance to the element, travels the shorter distance to the observation point. Thus, the difference in path lengths is partially compensated for, and the rays do not get very much out of phase. For the observation point 2, however, the situation is reversed; the ray which travels the longer distance from the plane to the element travels the longer distance to the observation point. If, as in the illustration, the molecular dimensions are something less than a wavelength, the path difference will be such as to produce a phase lag that will result in destructive interference of the two rays. Thus, it may be seen that the interference effect produces an all round decrease in intensity and that destructive interference will be more probable between rays scattered in the backward direction. There is, as a result, a dissymmetry in the angular distribution of intensity. This dissymmetry can be interpreted to give information regarding the size and shape of the dissolved polymer molecules. The relation of this effect to the characteristic dimension of the molecule has been calculated by DEBYE [10] for spherical, rod-like and randomly coiled particles in extremely dilute solution.

The experimental procedure consists of measuring the ratio of the relative intensities of the light scattered at two different angles from a solution of the particles. The expression for the ratio of the intensities $I_1$ and $I_2$ measured at angles $\theta_1$ and $\theta_2$ (measured backward from the direction of the beam) has been calculated for each of the above models. If we define a dissymmetry coefficient $q$ as $q = I_1/I_2 - 1$, then by measuring this coefficient it is possible, from theoretical relations, to evaluate either $L$, the length of the rods, or $\sqrt{\overline{r^2}}$, the root mean square distance between the ends of a randomly-coiled chain, according to the model assumed for the particles. The calculations are exact as long as the particles actually conform to the models assumed for them and if the particles scatter light independently of each other. The latter condition is realized by extrapolating the dissymmetry coefficient to infinite dilution.

The method has been applied to a number of polymers. The general correctness of the procedure was established by its application to solutions of tobacco mosaic virus,[11] which is known from other investigations to be rod shaped. The length of the molecule from dissymmetry measurements was found to be 2700 Å, in close agreement with the average value of 2900 Å obtained from electron micrographs on the same sample. Turbidity measurements at 90° to the incident beam, after certain corrections, gave a molecular weight of 41 million, which checks satisfactorily with that obtained from electron microscopy (39 million).

Polystyrene fractions with molecular weights from 2 to 10 million possessed the shape of a random coil. The value for $\sqrt{\overline{r^2}}$, the root mean separation of the ends of the polystyrene chain, calculated from the measured $q$, was found to be at least 3·7 times as large as that derived from a completely random configuration (that is, ideal calculation of a random walk in three dimensions). This may be accounted for by two factors. One is the finite cross section of the polystyrene chain, which prohibits its crossing back on itself, such as is possible in a random coil ; the other is the steric hindrance of the bulky phenyl side group, which restricts the relative orientations of the valence bonds. In the case of cellulose acetate, STEIN and DOTY [12] found that a low molecular weight fraction ($m = 52{,}000$), which would have a length of 1000 Å in the fully extended state, actually exhibits approximately this length in acetone solutions. Longer chains of cellulose acetate showed an increasing tendency to curl up; a high molecular weight fraction ($m = 170{,}000$) giving a maximum length of 1500 Å, whereas the length of the fully extended chain amounted to about 3000 Å. These conclusions are in agreement with viscosity and ultracentrifuge measurements on this polymer.[13]

## SEDIMENTATION AND DIFFUSION

Solid particles, suspended in a liquid, sediment in a gravitational field with a velocity determined by Stokes's Law. Measurement of the rate of sedimentation enables the mean size and the size distribution of the particles to be determined. When the particles are of colloidal size, the rate of sedimentation is very slow, and in order to observe and measure sedimentation, it is necessary to use fields much greater than gravity. The high speed ultracentrifuge developed by SVEDBERG and his collaborators[14] produces fields up to one million *g*, and observations may be made on macromolecules in the same way as with coarse dispersions in a gravitational field. The method is, however, difficult to operate and requires costly equipment which precludes its general use as a tool for the study of macromolecules. A complete account of this remarkable development has been published recently in book form,[14] and is also adequately described in several review articles.[15] It is unnecessary to summarize this information here, and our considerations will be confined to a brief review of the nature of the information obtained from sedimentation and diffusion studies, with special reference to long chain molecules.

Two types of ultracentrifugal measurements requiring two distinct ranges of centrifugal force are in general use.

*Sedimentation Equilibrium*—In this method the dilute solution is centrifuged in a cell for a time long enough for equilibrium between sedimentation, produced by the centrifugal force, and diffusion, to be established. Concentration changes in the cell are measured either by light absorption or by change in refractive index of the solution. Under the equilibrium conditions the following equation is true for the molecular weight of each species of molecule

$$m = \frac{2RT \ln c_2/c_1}{(1 - V\rho)\omega^2(x_2^2 - x_1^2)} \quad . \quad . \quad . \quad . \quad (12)$$

$c_1$ and $c_2$ = concentrations at two points, distant $x_1$ and $x_2$ from axis of rotation

$V$ = partial specific volume of dissolved substance

$\rho$ = density of solvent

$\omega$ = angular velocity

If the material is homogeneous the plot of ln $c$ against $x^2$ gives a straight line of slope proportional to the molecular weight. If the plot is curved, this is evidence that the material is inhomogeneous, and only an average molecular weight may be determined. The type of average depends on the method of observation of the concentration gradient. Light absorption gives a weight average molecular weight, $\overline{m}_w$, whereas the refractive index method measures the $Z$ average molecular weight $\overline{m}_z$ defined by

$$\overline{m}_z = \frac{\sum\limits_i n_i m_i^3}{\sum\limits_i n_i m_i^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

*Rate of Sedimentation*—At very high speeds of centrifuging, a homogeneous macromolecular material dispersed in a solvent of different density will sediment with a fairly sharp boundary. The rate at which the boundary moves in the solution, and at constant temperature, is dependent only on the centrifugal acceleration, and when the rate is reduced to unit centrifugal field, Svedberg defines a sedimentation constant $s$ according to the equation

$$s = \frac{dx/dt}{\omega^2 x} = \frac{\ln x_2/x_1}{\omega^2(t_2 - t_1)}$$

where $x_1$ and $x_2$ are the distances from the axis of the mean boundaries at times $t_1$ and $t_2$. The sedimentation constant is a specific quantity for a given material and is determined by the viscosity of the solvent, the specific volume of the solution $V$, and the size, shape and state of solvation or aggregation of the suspended material. The intrinsic sedimentation constant $[s]$ may be defined as

$$[s] = \frac{s\eta V}{(1 - V\rho)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

and represents the sedimentation constant reduced to unit centrifugal acceleration, unit viscosity and unit density difference. $[s]$ is characteristic of the macromolecules and depends only on the size of the sedimenting particle. The sedimentation constant, combined with the diffusion constant or the frictional ratio (deduced from viscosity, dielectric relaxation or other measurements), provides an independent method for the determination of molecular weights. Thus, the frictional factor per mol, $F$, which is the frictional force exerted on $N_0$ (one mol) molecules in a medium of viscosity $\eta$, is given by the Einstein equation

$$F = \frac{RT}{\eta D} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

where $D$ is the diffusion constant.

Since $[s] = mV/F$, it follows from (15) that

$$F = m(1 - V\rho)/\eta_s s$$

and therefore

$$m = \frac{RTs}{D(1 - V\rho)} \quad . \; . \; . \; . \; . \; . \quad (16)$$

This is Svedberg's fundamental equation for the determination of molecular weights by sedimentation and diffusion measurements.

With some heterogeneous polymers, in sufficiently dilute solution, each molecular species sediments without interference from other species. If the $[s]$'s of the different species differ sufficiently and the diffusivity is not too great, a more or less sharp boundary forms for each species and the amount of each may be estimated. If the difference in molecular weights is small, diffusion causes overlapping of the boundaries, and the separate species cannot be determined by direct observation, although an analysis of the experimental data gives a size distribution curve. When diffusion is negligible, the spread of the sedimentation boundary is entirely due to differences in the sedimentation constants of the different molecular species, and a distribution of sedimentation constants may be determined. By combining this result with the relation between frictional factor and molecular weight (which can be most conveniently determined from diffusion experiments) a distribution of molecular weights may be calculated.

The molecular weight obtained by the use of equation (16) depends upon a knowledge of three constants of the substance under examination—*viz* the sedimentation constant $s$, the diffusion constant $D$, and the partial specific volume $V$. Constants $s$ and $D$ vary with molecular weight, but $V$ could be assumed to be independent of it. It is therefore possible to treat $s$ or $D$ as variable instead of $m$, and just as we have already found with $m$, different experimental methods give different averages for $s$ or $D$. Thus, it is possible to define $s_n$, $s_w$ and $s_z$, and $D_n$, $D_w$ and $D_z$ respectively by analogy with equations (6), (7) and (13). Molecular weights calculated from equation (16) by means of these average values are denoted by double subscripts—*e.g.* $\bar{m}_{nw} = \frac{RT}{1 - V\rho} \cdot \frac{s_n}{D_w}$. Nine different values of $\bar{m}$ could be obtained by different combinations, together with many others of intermediate value. These averages are, in turn, related to the shape of the dissolved molecules, and for a complete discussion of this subject reference should be made to the papers of SINGER [16] and GRALEN.[17]

*Measurement of Molecular Constants*—Most of the measurements using the ultracentrifuge have been carried out on proteins and viruses in aqueous solution, and these have proved to be very suitable material for its successful application. These molecules are, with the exception of some of the viruses and nucleo-proteins, spheroidal or ellipsoidal in shape, in contrast to the synthetic high polymers and natural products such as cellulose and rubber, which are of the thread type of structure, and thus may assume a variety of configurations in solution. Because of their shape, linear polymers show appreciable interaction at concentrations in which protein molecules behave as separate entities. This, and other experimental and theoretical difficulties, impose at the present time severe limitations on the use of these methods in the study of linear polymers. As with other properties, the theoretical laws are only strictly applicable to infinitely dilute solutions, in which all molecules act independently. It is therefore necessary to extrapolate the measured sedimentation and diffusion constants to infinite dilution. While this presents no difficulty with most of the proteins, the concentration dependence of $s$ and $D$ for high polymers renders this extrapolation difficult. The particle interaction persists even at the lowest concentrations usable for experiment. It is mainly for these reasons that ultracentrifugal methods have not proved so useful an experimental tool in the field of high polymers as they have with the proteins.

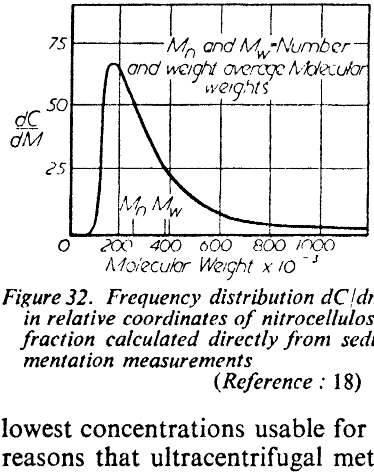

*Figure 32. Frequency distribution dC/dm in relative coordinates of nitrocellulose fraction calculated directly from sedimentation measurements*
(*Reference* : 18)

The study of the long, thread-like molecules of cellulose and its derivatives is beginning to yield results of interest. *Figure 32* shows the distribution curve obtained in Svedberg's laboratory for a nitrocellulose fraction from sedimentation measurements.[18] The different average molecular weights are indicated on the diagram. The $\bar{m}_n$ values were obtained by means of the osmotic balance (see page 159).

Molecular weight values alone throw no light on the particle shape, but ultracentrifugal studies have the additional merit that they can be interpreted to give some knowledge of the average shape of the polymer molecules. The frictional factor $F$ or the frictional coefficient $f$ $(=\eta F)$ may be determined from the sedimentation constant, $s$

$$f = \eta F = \frac{m(1 - V\rho)}{s}$$

This value may be calculated for spherical particles of molecular weight $m$ by the use of Stokes's Law $(f = 6\pi\eta r)$. The frictional coefficient $f$ for non-spherical molecules is always greater than that of spherical molecules $(f_0)$ of the same volume. Svedberg has therefore introduced the frictional ratio $f/f_0 (= F/F_0)$, called the asymmetry coefficient, which can be expressed in terms of the axial dimensions of the equivalent ellipsoid. The more the ratio $f/f_0$ deviates from unity, the larger will be this axis ratio. This representation has proved extremely successful in protein studies, but it has not yet been used systematically on solutions of fractionated polymers of known average molecular weight.

*Table XVIII* gives the values of $f/f_0$, $l$, $d$ and $l/d$ for cellulose nitrate determined from sedimentation velocity and diffusion measurements, and $l/d$ from specific viscosity measurements using Burgers's formula (page 164). It also contains values of the lengths of stretched molecules calculated from $m_w$ and $m_{nw}$ ($l_w$ and $l_{nw}$), together with some values of $l$ from streaming birefringence experiments.

*Table XVIII*

*Axial Ratios and Lengths of Nitrocellulose Molecules Determined by Various Methods*

| *Nitrocellulose fraction* | $f/f_0$ | *Sedimentation and diffusion* | | | $[\eta]$ | *Molecular weight* | | *Streaming birefringence* |
|---|---|---|---|---|---|---|---|---|
| | | $l/d$ | $l(\text{Å})$ | $d(\text{Å})$ | $l/d$ | $l_w(\text{Å})$ | $l_{nw}(\text{Å})$ | $l(\text{Å})$ |
| *e.h.e.* | 6·1 | 230 | 2,900 | 13 | 260 | — | 5,100 | 3,000 |
| *VF* 120 | 4·2 | 110 | 1,200 | 12 | 150 | 1,600 | 1,700 | 1,800 |
| *VF* 3 | 2·7 | 42 | 450 | 11 | 88 | 370 | 530 | 550 |
| *VF* 2 | 2·2 | 24 | 240 | 10 | 59 | 350 | 270 | — |
| *Lnt* | 4·6 | 130 | 1,700 | 13 | 210 | 2,700 | 3,000 | 2,100 |
| *Hnt* | 4·2 | 110 | 1,300 | 12 | 190 | — | 1,800 | 2,400 |
| *Mpt* 128 | 6·1 | 230 | 3,600 | 16 | 350 | 7,300 | 9,400 | — |
| *AF* 1 | 2·2 | 26 | 270 | 10 | 67 | 460 | 330 | — |
| *FK* 2 | 5·6 | 190 | 2,600 | 14 | 250 | 4,400 | 5,100 | 2,700 |
| *FK* 2*a* | — | — | — | — | 240 | — | — | 2,500 |
| *FK* 3 | 5·8 | 210 | 2,800 | 13 | 250 | 5,200 | 5,400 | 3,100 |
| *FK* 3*a* | — | — | — | — | 240 | — | — | 3,800 |
| *FK* 6 | 5·5 | 190 | 2,300 | 12 | 290 | 2,600 | 3,300 | 2,800 |
| *FK* 9 | 10·4 | 650 | 9,600 | 15 | 520 | — | 21,000 | — |

A detailed comparison of the results obtained by the various methods should be avoided, in view of the nature of the theoretical approximations implied in the application of different methods. The results as a whole, however, demonstrate that the cellulose nitrate molecule approximates closely in shape to that of an elongated and rigid rod. This shape, as much other work has shown, is characteristic of cellulose and its derivatives.

## OSMOTIC PRESSURE

The measurement of the osmotic pressure of dilute solutions is the most commonly used method for determining the molecular weights of macromolecules. The use of the more facile intrinsic viscosity/molecular weight relationships is almost invariably based on osmotic determinations of the molecular weights of well fractionated samples. The osmotic pressure method is not, however, straightforward, since apart from the necessity for accurate measurement of the small osmotic pressure produced by high molecular weight materials, polymer solutions, as we have already seen, show very marked deviations from ideal behaviour. According to the classical van't Hoff law, the osmotic pressure of a dilute ideal solution is given by

$$\frac{\Pi}{c} = \frac{RT}{m} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

where $\Pi$ = osmotic pressure, $c$ = concentration, $m$ = molecular weight of the solute, $R$ = gas constant, $T$ = absolute temperature. If this law holds, $\frac{\Pi}{c}$ should be independent of $c$ and equal to $\frac{RT}{m}$. It does, in fact, hold for solutions of small molecules up to concentrations of several per cent, but a large number of measurements on high polymer solutions show marked deviations from van't Hoff's law at all finite concentrations. The plot of $\Pi$ is not parallel to the $c$ axis, as required in the ideal case, but is generally a line bending upwards from the $c$ axis. As an illustration of this behaviour, *Figure 33* shows the dependence of the osmotic pressure on concentration of solutions of polyisobutylene fractions in cyclohexane.[19] With the same polymer in a series of solvents, a similar plot gives lines of different slopes, but the limiting value of $\frac{\Pi}{c}$ at infinite dilution is the same with all solvents. No exception to this behaviour has been found, although with very high molecular weight material exhibiting a steep slope of the curve, it is not always possible to demonstrate this with certainty. The extrapolation error can, however, be reduced by suitable choice of solvent, which gives a small dependence of $\frac{\Pi}{c}$ on $c$.

The reasons for the deviation from ideality have been discussed in the previous chapter. Thermodynamically, for dilute solutions of any solute

$$\Pi \bar{V}_1 = -\Delta \bar{G}_1 = T\Delta \bar{S}_1 - \Delta \bar{H}_1 \quad . \quad . \quad . \quad (18)$$

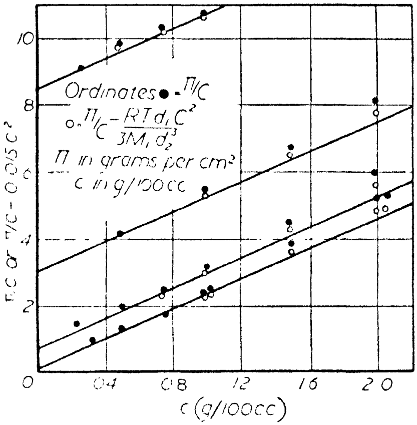

*Figure 33. Dependence of osmotic pressure on concentrations for solutions of polyisobutene in cyclohexane at 25°C*
(*Reference* : 20)

where $\bar{V}_1$ is the partial molar volume of the solute, $\Delta \bar{G}_1$, $\Delta \bar{S}_1$, and $\Delta \bar{H}_1$ are the partial increases in free energy, entropy and heat content when one mol of solvent is added to a large bulk of solution. The non-ideal behaviour is due primarily to deviations from ideality of the entropy of mixing, $\Delta \bar{S}_1$, rather than to the heat of mixing effect, although the latter is not always negligible. The relationships for the heat, entropy, and free energy of mixing of chain molecules with small molecules have been previously deduced, and if the expression for $\Delta \bar{G}_1$ (equation 31, Chapter 4) is introduced into equation (18) we obtain

$$\frac{\Pi}{v_2} - \frac{RTv_2^2}{3\bar{V}_1} = \frac{RT}{\bar{V}_2} + \frac{RT}{\bar{V}_1}\left(\frac{1}{2} - \mu\right) v_2 \quad . \quad . \quad (19)$$

This expression was first proposed by HUGGINS [20] and if concentrations expressed are in grams of solute ($c_2$) per cubic centimetre of solution the corresponding equation is

$$\frac{\Pi}{c_2} - \frac{RT}{3m_1} \cdot \frac{d_1c_2^2}{d_2^3} = \frac{RT}{m_2} + \frac{RTd_1}{m_1d_2}\left(\frac{1}{2} - \mu\right) c_2 \, . \quad . \quad (20)$$

where $d_1$ and $d_2$ are the densities and $m_1$ and $m_2$ are the molecular weights of the components.

If it is assumed that the solution is so dilute that polymer/polymer contacts are negligible, further dilution does not change the number or nature of the intermolecular contacts, so that $\Delta \bar{H}_1 = 0$. Then for these solutions, the entropy expression (equation 18, Chapter 4) becomes

$$\frac{\Delta\bar{S}_1}{R} = \frac{\bar{V}_1}{\bar{V}_2} . v_2 + \left(\frac{1}{2} - \frac{1}{z'}\right) v_2^2 + \ldots,$$

and this reduces to

$$\frac{\Delta\bar{S}_1}{R} \approx \frac{N_2}{N_1} \approx R . \frac{\bar{V}_1}{m_2} c_2 \quad . \quad . \quad . \quad . \quad . \quad (21)$$

It follows, therefore, as pointed out by GEE,[21] that by comparing equations (18) and (21), van't Hoff's law is seen to be the correct limiting law at infinitely dilute solution, whatever may be the size and shape of the molecules.

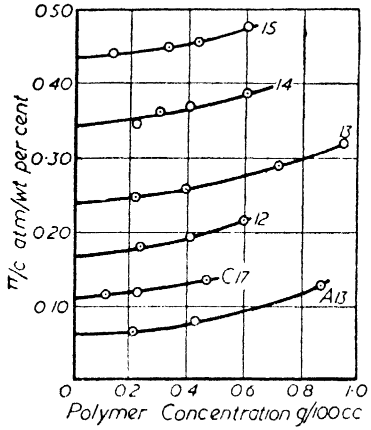

*Figure 34. Dependence of osmotic pressure on concentration for solutions of polymethyl methacrylate fractions in benzene at 25°C*
(*Reference* : 22)

From any set of measurements of the osmotic pressure of a given solution at different concentrations, the plot of the expression on the left hand side of equation (20) against $c_2$ should yield a straight line. The intercept on the ordinate ($c_2 = 0$) gives directly the molecular weight of the solute ($\mu$ can also be computed from its slope).

The validity of equation (20) has been demonstrated in many osmotic pressure studies.[20] The second term on the left hand side of the equation is usually negligible at most concentrations at which osmotic pressure measurements are made, thus explaining the rectilinear relationship between $\pi/c_2$ and $c_2$ often obtained. The upward curvature of the plot in the case of polyisobutylene in cyclohexane [19] (*Figure 33*) and polymethyl methacrylate in benzene [22] (*Figure 34*) are instances in which the second term is effective. Under these conditions equation (20) reduces to a commonly used form of the osmotic equation

$$\Pi = \frac{RT}{m_2} . c_2 + Bc_2^2 \quad . \quad . \quad . \quad . \quad . \quad (22)$$

where $B$ is a constant $\left[= \frac{RT}{m_1} \cdot \frac{d_1}{d_2^2} \cdot \left(\frac{1}{2} - \mu\right)\right]$ which characterizes each polymer/solvent system.

Two techniques are available for the measurement of osmotic pressure, the static and dynamic methods. In the former the liquid head developed by the influx of solvent into the solution through a suitable semi-permeable membrane is measured, whereas in the dynamic method the magnitude of an externally applied pressure, necessary to counteract the osmotic pressure, is determined. In recent years a considerable number of individual osmometers of both types have been described in the literature.[23] The principal advantage of the dynamic method is the rapidity with which the measurement can be made, although the static method is probably more precise. In order to secure the advantage of rapidity of measurement it is necessary to employ a large membrane which must be adequately supported to prevent ‘ ballooning ’ effects.

In its modern form the osmometer is usually constructed of metal, preferably stainless steel for all purpose usage, the membrane being held vertically between heavy metal blocks in which shallow annular grooves have been cut, the edges of which support the membrane. The cells containing the grooves, which may be as large as 6 in in diameter, connect through fine drilled holes to chambers which lead, through metal glass seals, to glass capillary tubes. In order to avoid contamination by grease, metal needle valves are used for filling and emptying the cells.

Suitable semi-permeable membranes are usually made by controlled denitration of nitrocellulose film by swelling commercial cellulose sheet or by bacteriological methods.[57] Various treatments are described for swelling sheets [24] to suitable pore size, but the preparation and conditioning of membranes are very much a matter of experience, which can be attained only by trial and error, until suitable conditions of strength and permeability have been fixed.

The results of the osmotic method become doubtful if the molecular weight is less than 10,000 or if the polymer contains fractions with molecular weight below this limit, since low molecular weight materials diffuse through denitrated cellulose membranes. With special precautions diffusion may be reduced, and FLORY [19] has measured molecular weights as low as 6,000 with swollen cellophane membranes. In the high molecular weight range the osmotic method becomes difficult on account of the low osmotic pressure of the solution. Molecular weights of one million or more cannot be determined with any precision, and the most favourable range is probably from 40,000 to 500,000. Recently, SVEDBERG and JULLANDER [25] have described an osmotic balance by means of which the weight instead of the height of the column of solution is measured. By the use of an ordinary analytical balance they were able to weigh a difference in height of 0·01 mm, compared with an accuracy of 0·1 mm attained in the best determination based on direct liquid height measurements. This new development may result in a considerable increase in the accuracy of osmotic pressure measurements in the low concentration range, and with very high molecular weight materials.

## MOLECULAR WEIGHT DETERMINATION BY OTHER METHODS

This section would not be complete without reference to certain other methods of molecular weight determination, which, although not of a general nature, have their special and important uses.

*Cryoscopic Methods*—The method of the lowering of the freezing point (or the elevation of the boiling point) which has proved so useful in the determination of the molecular weights of small molecules is limited in its application in the polymer field to molecular weights not greater than 5,000–6,000. The difficulty in extending this range is one of sensitivity of measurement of small temperature changes and the necessity of using relatively concentrated solutions in order to obtain measurable freezing point depression. The van't Hoff law for dilute solutions, which assumes the validity of Raoult's law, may be expressed by the equation

$$-\ln N_1 = \frac{L_F}{RT_0^2} \cdot \theta$$

where $N_1$ is the mol fraction of the solvent in solution
$T_0$ is the freezing point of the solvent
$\theta$ is the freezing point depression
$L_F$ is the molar latent heat of fusion of solvent.

Expanding the logarithm and assuming dilute solution, $-\ln N_1 \simeq \frac{m_1}{m_2} \cdot w$, where $w$ is the weight fraction of polymer in the solution and $m_1$ and $m_2$ are the molecular weights of solvent and polymer

$$\left(\frac{L_F}{T_0}\right)\frac{\theta}{w} = \frac{m_1 R T_0}{m_2} \qquad . \quad . \quad . \quad . \quad . \quad . \qquad (23)$$

Since Raoult's law does not hold for polymer solutions except at infinite dilution, equation (23) must be corrected, as with the osmotic pressure expression, by the addition of a term $B'w$ to the right hand side, where $B'$ depends on the solvent, but not on molecular weight. It is therefore necessary to extrapolate all measurements to infinite dilution.

The cryoscopic data for polystyrene fractions at different concentrations in benzene [26] are plotted in *Figure 35*. Deviations from

Raoult's law are appreciable for molecular weights greater than 1,000. As with osmotic pressure measurements, cryoscopic data give a number average molecular weight.

*End Group Determinations*—It has already been shown in Chapter 2 that, in the case of linear condensation polymers possessing terminal carboxyl or amino groups, determination of the end group by a titration or other chemical method gives a simple, yet accurate, determination of the molecular weight. The sensitivity of the method decreases with increase in molecular weight. It is now a well established fact that, in free radical initiated polymerization, the radical or fragments of the radical attach themselves to the end of the polymer chain. Recently EVANS and his co-workers[27] have applied this method to the determination of high molecular weight addition polymers. Using OH radicals as initiators with methyl methacrylate, acrylonitrile and other monomers, they were able to prepare macromolecules with OH groups at each end of the chain. The number of OH groups was determined by a micro method based on the reaction of methylmagnesium chloride and a hydroxy compound. The molecular weights obtained were in close agreement with osmotic determinations on the same samples.

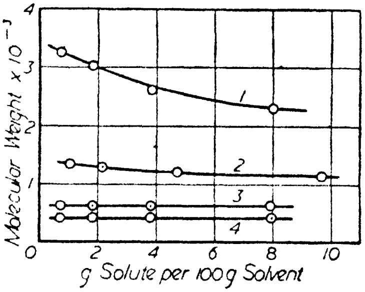

*Figure 35. Effect of concentration on cryoscopic molecular weight of polystyrene fractions in benzene* (*Reference* : 26)

Since methods of end group determination virtually count the number of molecules, the molecular weight obtained is a number average, $\overline{m}_n$.

# IV

## VISCOSITY OF SOLUTIONS OF MACROMOLECULES

A characteristic property of long chain molecules is the high viscosity of their solutions. Viscosity measurement is one of the simplest to make with reasonable accuracy, and it is probably for this reason that more researches have been carried out on the viscosities of solutions of macromolecules than on any other physical property. Apart from the purely experimental conditions of measurement, three factors are fundamental in determining the viscosity of a dilute polymer solution: *a* the chemical nature of the solvent and solute, which includes their interaction and thus the solvation or aggregation, *b* the concentration of the solute and *c* the molecular weight of the solute for a homogeneous polymer or the molecular weight distribution for a heterogeneous polymer. The influence of these factors on the configuration of the macromolecules and their application in the determination of molecular weights will be considered in subsequent sections.

*Definition and Symbols*—The increase in viscosity $\eta$ of a polymer solution over that of the pure solvent $\eta_0$ is expressed as a fraction, called the specific viscosity $\eta_{sp}$, according to

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \eta_r - 1$$

where $\eta_r$ is termed the 'relative viscosity' and is equal to $\frac{\eta}{\eta_0}$. The specific viscosity is dependent on the concentration, and in order to define a quantity characteristic of a given macromolecule in a solvent it is necessary to take the initial slope of the $\eta_{sp}$ *versus* concentration curve, *i.e.*

$$\lim_{c \to 0} \eta_{sp}/c = \lim_{c \to 0} \frac{\ln \eta_r}{c} = [\eta]$$

This limiting value of $\eta_{sp}/c$ at infinite dilution was termed by KRAEMER[28] the 'intrinsic' viscosity. The value of $\eta_{sp}/c$ at any other concentration is often referred to as the 'reduced viscosity'. Kraemer also pointed out that the logarithmic form of $\eta$ was less dependent on $c$ than $\eta_{sp}/c$, and thus is a more convenient form of the equation to use for extrapolation purposes.

Since the intrinsic viscosity has the dimensions of a specific volume, concentrations should be expressed theoretically on a volume basis, but since they cannot be evaluated easily in practice, because of the unknown density of the polymer particles, it is preferable to use weight per unit volume. It has now become almost general practice to take 100 cc as the unit of volume and thus $[\eta]$ is expressed as 100 cc solution/g units.

## VISCOSITY AND PARTICLE SHAPE

When the molecules of the solute are very large in comparison with the solvent molecules, the usual thermal motion in liquids is inapplicable to them, and their influence on the viscosity of the mixtures originates in a different mechanism from that which applies to simple solutions. The character of the viscous flow of the solvent is modified, and the viscosity may be regarded as a distortion of the lines of flow of the continuous solvent around the suspended particles. The solute particles block the steady motion of some of the solvent molecules, and thus produce an increase in viscosity. In 1906 EINSTEIN[29] treated theoretically the case of a dilute solution containing spherical particles and showed that the specific viscosity was independent of the size of the particles and dependent only on the volume fraction of the solute. He deduced the now well known formula

$$\eta_{sp} = 5/2\,v$$

where $v$ = volume fraction of the solute.

The Einstein equation formed the starting point of many attempts to take into account the deviations from spherical shape, and equations were derived by hydrodynamical methods, for ellipsoidal and rod-shaped particles. According to the above equation, the specific viscosity is dependent on the total volume of the particles. A very large amount of experimental data on the viscosities of macromolecules of different molecular weights shows that the viscosity depends on molecular weight and often increases rapidly with increase in molecular size. One may make the reasonable assumption that this is connected with deviations from spherical shape; the length to diameter ratio will increase with molecular size. Considering a chain molecule, two extreme forms of the molecule may be imagined: *a* a completely extended chain of monomer units, *b* a tightly folded up chain which may have an almost spherical or ellipsoidal shape. For equal molecular weights it is clear that the resistance offered to solvent flow would be greater for solutions of the extended molecules than for the compact molecules. Further, if the molecules exhibit strong Brownian movement in solution, the volume swept out by the chain molecules will be very large compared with that of spherically shaped molecules. A simple, though approximate, calculation shows that, for a molecule containing $10^5$ unit spheres, each of radius $10^{-7}$ cm, the effective volume of a linear structure is about 1000 times that obtained when the units are packed into a sphere. We must thus expect strong intermolecular action in solutions of extended molecules at concentrations at which spherical molecules would be free. Another important difference due to the molecular shape factor is the orientation of the asymmetrical particles under flow. At sufficiently high rates of shear, long rigid particles would be orientated in the direction of shear, with a resulting diminution in viscosity and the appearance of birefringence when examined between crossed polaroids. For elongated structures a proportionality between rate of shear and birefringence would be expected, and this behaviour has been observed with nitrocellulose and polystyrene solutions. Globular proteins, on the other hand, show no orientation or birefringence in streaming solutions.

Several equations connecting viscosity in dilute solution and the axial ratio of the solute molecules have been derived hydrodynamically. For rod-like particles showing strong Brownian movement (that is, no orientation), and with an axial ratio ($f$) much larger than unity, SIMHA [30] deduced the equation

$$\eta_{sp}/v = \frac{f^2}{15(\ln 2f - 3/2)} + \frac{f^2}{5(\ln 2f - 1/2)} + \frac{14}{15} \quad . \quad (24)$$

BURGERS,[31] from a detailed hydrodynamical study, has derived a relation for very long, rod-like particles with slight orientation, which was identical with the equation of Simha with the second and third terms omitted.

Many other equations have been derived for the viscosity of rod-like particles in dilute solution, and in all cases they take the form

$$\eta_{sp}/v = K \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

where $K$ depends on the type of particle. For spherical particles $K = 2{\cdot}5$, while for very long rod-like particles $K$ is equal to the right hand side term of equation (24). These equations may therefore be used to calculate the average axial ratio from the values of $\eta_{sp}/v$ extrapolated to infinite dilution.

*Table XIX* shows the mean axial ratio calculated by CAMPBELL and JOHNSON [32] from viscosity data for nitrocellulose in acetone. The molecular weights were determined from Staudinger's equation, using an experimentally determined proportionality constant. The

*Table XIX*

*Nitrocellulose/Acetone System* [32]

| *Molecular weight (viscosity)* | *Mean axial ratio* | | *Molecular weight calculated from axial ratio (Burgers)* |
|---|---|---|---|
| | *Simha's equation* | *Burgers's equation* | |
| 25,000 | 26 | 52 | 47,400 |
| 87,000 | 54 | 108 | 98,500 |
| 107,000 | 61 | 120 | 109,000 |
| 157,000 | 76 | 151 | 137,000 |
| 219,000 | 91 | 183 | 167,000 |
| 346,000 | 118 | 216 | 197,000 |

last column gives the molecular weights calculated from the axial ratio obtained by Burgers's equation assuming an extended straight chain of nitrated cellobiose units. The results are in general agreement with the view that the nitrocellulose molecule possesses a fairly rigid, rod-shaped structure at low molecular weights, but there are indications that large molecules tend to assume less extended or coil shaped forms. This viewpoint is strongly supported by recent studies of BADGLEY and MARK [33] on cellulose acetate. These results are listed in *Table XX*, and are consistent with the viewpoint that the cellulose acetate molecule consists of a relatively extended molecule, but that as the molecule becomes larger it becomes more and more curled up. A relatively high rotational restriction between adjacent segments would be expected for the cellulose derivatives on purely stereochemical grounds.

*Table XX*

*Cellulose Acetate/Acetone System* [33]

| *Molecular weight* $m_n$ *(osmotic pressure)* | $[\eta]$ | *Length* (X-*ray*) | *Dimensions from viscosity measurements* (*Simha*) | |
|---|---|---|---|---|
| | | | *Length* (*Å*) | *Diameter* (*Å*) |
| 360,000 | 3·45 | 6,920 | 1,861 | 20·4 |
| 275,000 | 3·29 | 5,300 | 1,676 | 18·8 |
| 230,000 | 3·16 | 4,430 | 1,556 | 17·9 |
| 158,000 | 2·60 | 3,040 | 1,285 | 16·3 |
| 133,000 | 2·23 | 2,560 | 1,130 | 15·7 |
| 99,000 | 1·73 | 1,910 | 938 | 15·1 |
| 52,000 | 1·10 | 1,000 | 628 | 13·4 |
| 31,000 | 0·65 | 595 | 434 | 12·4 |

Some corroborating evidence for these conclusions is obtained from the experiments of STEIN and DOTY [12] on the angular dependence of light scattering for cellulose acetate. The data are given in *Table XXI.* It may be seen that the dimensions of the three low molecular weight fractions correspond within experimental error to the calculated values for extended molecules, but that for the two high molecular weight products the dimensions are considerably less than for the completely stretched out molecule.

So far we have considered the theory of viscosity of polymer solutions in terms of rigid shapes of the suspended particle (molecule), the axial ratio of which may be calculated from the experimental data. Many of the molecules in which we are interested have randomly coiled forms, in which the average distance between the ends may be calculated from equations (3) and (5). The

*Table XXI*

*Dimensions of Cellulose Acetate Molecules*[12]

| *Molecular weight of fractions (osmotic pressure)* | *Root mean square distance between ends (light scattering)* | | *Calculated from molecular weight for extended molecule* |
|---|---|---|---|
| | *Assuming random rods* (*Å*) | *Assuming rigid coils* (*Å*) | (*Å*) |
| 163,000 | 1,900 | 1,340 | 3,100 |
| 135,000 | 1,900 | 1,340 | 2,400 |
| 75,000 | 1,550 | 1,120 | 1,440 |
| 65,000 | 1,550 | 1,120 | 1,250 |
| 52,000 | 1,380 | 960 | 1,000 |

particular case for large solute molecules built up of $n$ hydrodynamic units has been treated by HUGGINS[34] and DEBYE,[35] who have deduced that

$$\eta_{sp}/c = kn$$

Since the number of atomic groups is proportional to the molecular weight, this treatment results in a linear relationship between intrinsic viscosity and molecular weight. This form of relationship was discovered empirically by STAUDINGER,[36] and is approximately true for many types of long chain molecule. Its application for the evaluation of molecular weights will be considered on p. 172 *et seq.* The general equations of Huggins and Debye allow of the evaluation of the constant $k$ in terms of molecular magnitudes. In principle, then, it should be possible to calculate the constant in Staudinger's law. The correspondence between theory and experiment is, however, not good. This is not surprising when we realize that polymer chains may be stiffer than provided for by the model based on free rotation of adjacent groups, and that interaction between parts of the chain may not be negligible.

### DEPENDENCE OF VISCOSITY ON CONCENTRATION

In the foregoing treatment of the theoretical viscosity equations the intrinsic viscosity was found to be independent of concentration. This is so because, in the derivation, solute/solute interaction was neglected. These relationships must therefore be considered as strictly true only at infinite dilution. The inclusion of interaction effects[37] in the case of spherical particles led to the introduction of a term in $v^2$, namely

$$\eta_{sp} = 2{\cdot}5v + 14{\cdot}1v^2$$

and this equation was shown to hold at much higher concentrations than the linear Einstein equation. Since, as we have already seen, interaction between asymmetric particles is much greater than with spheres, it is to be expected that the concentration dependence of $\eta_{sp}/c$ will be important at much lower concentrations than with spherical particles. This is generally observed experimentally, as is shown clearly in *Figure 36*, which gives the plot of $\eta_{sp}/c$ against $c$ for a series of polystyrene fractions.[38] The different molecular weight fractions give a series of straight lines of slope $a_2$, which increases with molecular weight, and all obey a relationship of the form

$$\eta_{sp}/c = [\eta] + a_2 c \quad (26)$$

The first coefficient $[\eta]$ is the intrinsic viscosity and is clearly a measure of the viscosity behaviour at infinite dilution. The second term reflects the interaction amongst solute molecules, and in many cases for not too high concentrations it has been found [38] that

$$a_2 = k'[\eta]^2$$

where $k'$ is a constant which varies with the polymer and solvent, but is independent of molecular weight. The value of $k'$ is usually between 0·30 and 0·40 for linear polymers in good solvents.

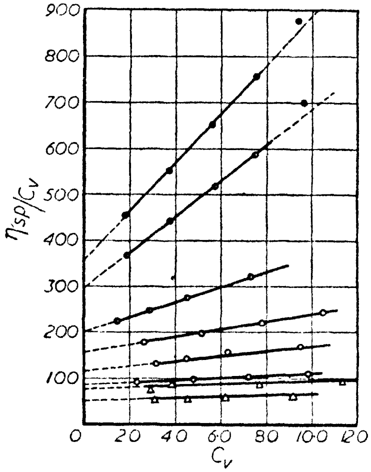

*Figure 36. Dependence of viscosity on concentration for a series of polystyrene fractions (Volume concentration in cc of solute per litre solution) (Reference : 50)*

The above equation can therefore be expressed

$$\eta_{sp}/c = [\eta] + k'[\eta]^2 c \quad . \quad . \quad . \quad . \quad . \quad (27)$$

Other relationships have been proposed to explain the variation with concentration of the viscosity of polymer solutions, and most of them can be reduced to a form closely approximating to equation (27). Thus, the equation of MARTIN [39]

$$\eta_{sp}/c = [\eta]e^{k'[\eta]c}$$

which has been widely used and is generally applicable over a concentration range up to 5 per cent polymer, reduces to equation (27) on expanding the exponential and ignoring higher concentration terms.

### EFFECT OF SOLVENT ON VISCOSITY

The intrinsic viscosity of dilute solutions of a given high polymeric substance varies with the nature of the solvent. Flexible linear polymers exhibit higher intrinsic viscosities in good solvents than in poor solvents. In any series of good solvents, however, the intrinsic viscosity is fairly constant, which indicates that the shape of the macromolecule is similar in these solvents. The behaviour of different polymers varies in a markedly different manner towards change of solvent or solvent composition. As we shall see later, the highly flexible polystyrene shows a marked contrast in solvent behaviour to the more rigid cellulose derivatives.

The variations of the intrinsic viscosity with composition may, according to MARK *et al.*,[40] be interpreted in terms of the types of interaction between solute and solvent molecules. If the polymer mixes with the solvent without heat change—that is, there is no attractive or repulsive force acting between them—all configurations of the polymer molecule in solution will have the same energy. If, on the other hand, dissolution of the polymer is an endothermic process, the macromolecules will be surrounded by an energetically unfavourable solvent, and will thus attract each other in solution and squeeze out the solvent from between them. Thus, with flexible chain molecules, configurations which involve contact of the molecule with itself will be promoted and the molecule will take up a more coiled and contracted shape. In a good solvent, which is energetically favourable, the opposite will be true, and the polymer molecule will interact strongly with the solvent and become, in the limiting case, surrounded by a solvated hull. This would tend to prevent polymer/polymer contacts and the molecule would take on a more extended configuration. Since an extended form is associated with a high intrinsic viscosity, a flexible molecule, other things being equal, will exhibit a high intrinsic viscosity in a good solvent and a low intrinsic viscosity in a poor solvent.

We have already seen that the change of viscosity with concentration may be represented by the equation

$$\eta_{sp}/c = [\eta] + k'[\eta]^2 c$$

where $k'$ is a constant for a given chemical species in a given solvent. The initial slope of the $(\eta_{sp}/c)/c$ curve, which has the value $k'[\eta]^2$, is a function of the solvent (*Figure 37*), and this will depend on the nature of the polymer/solvent interaction. It should therefore be possible to make some predictions from the slope and limiting intercept of the $(\eta_{sp}/c)/c$ curve of the interaction energy between solvent and polymer, and of the influence of solvent composition on the shape of the dispersed macromolecules.

These effects should be pronounced for polymer molecules of high flexibility and uniform molecular structure. Thus polystyrene[40] shows a high intrinsic viscosity in good solvents and a low value in poor solvents. Other results[41] show that there is a similar regular decrease in $[\eta]$ for polyisobutene as the solvent power decreases.

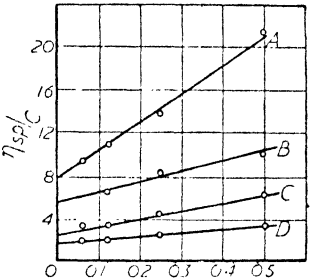

*Figure 37. Plot of viscosity data for polystyrene fraction in several solvents: A toluene, B ethylene dichloride, C methyl ethyl ketone, D methyl ethyl ketone/isopropanol*

(*Reference*: 11)

Valuable information may be obtained from viscosity measurements in mixed solvents, provided the measurements are carefully chosen. If a poor solvent (precipitating agent) is added to a good solvent, the solution is energetically less favourable than in the better solvent, and the mixed solution should exhibit a lower viscosity than for the same polymer in the pure solvent. *Figure 38* shows the results of ALFREY, JUSTICE and NELSON,[42] giving the variation of intrinsic viscosity of a polystyrene fraction in toluene with the addition of increasing amounts of butanol (precipitant). The curves at the three temperatures extrapolate to a common intrinsic viscosity at the precipitation point. The same extrapolated value of $[\eta]$ at the precipitation point was also observed with other precipitants added to toluene solution. The authors explain this in the following manner. Assuming that the characteristics which determine intramolecular agglomeration would also determine intermolecular association, then the point at which precipitation begins represents a definite intermolecular

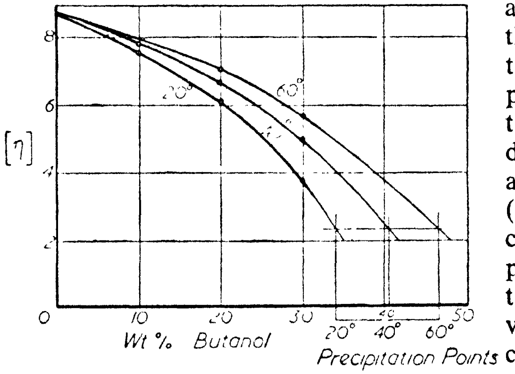

*Figure 38. Intrinsic viscosity of polystyrene fraction in toluene/butanol*

(*Reference*: 42)

agglomeration tendency of the chain segments of different molecules, and thus a certain intrinsic viscosity independent of the solvent/non-solvent mixture.

The experiments of FRITH[43] on polyvinyl acetate and polyvinyl chloride in mixed solvents indicate a different behaviour to that of polystyrene, as is evident from *Figure 39*. The limiting value of $\eta_{sp}/c$ or $[\eta]$ is independent of the solvent composition, but the slope of the curve is a function of the solvent, the steepest slopes representing the best solvents.

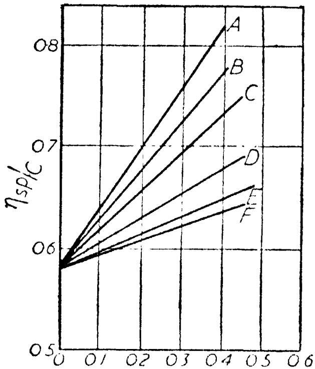

*Figure 39. Effect of solvent composition on the viscosity of dilute solutions of polyvinyl acetate in ethyl acetate/dimethyl phthalate mixtures at 25°C: A 90% D.M.P., B 7% D.M.P., C 50% D.M.P., D 30% D.M.P., E 10% D.M.P., F 100% E.A.*
(*Reference* : 43)

In the case of non-flexible chains such as cellulose derivatives, the alteration of solvent environment cannot be expected to produce marked changes in the configuration of the chains. It would not be anticipated that the intrinsic viscosity would vary greatly from good to poor solvents, and this is in agreement with the results of SPURLIN, MARTIN and TENNENT[44] for ethyl cellulose in a number of solvents. The slopes of the $(\eta_{sp}/c)/c$ curves, however, varied with solvent, but, contrary to Frith's observation, the steepest slopes represented the poorest solvents.

In spite of the somewhat conflicting conclusions, these results may be interpreted broadly in terms of two effects: *a* the configuration of the macromolecule as determined by polymer/solvent interaction; *b* the interaction and interference between the chains of separate molecules as the concentration increases. Highly flexible molecules would show different effects from stiff, rigid molecules, in both the slope and the intercept $[\eta]$ of the $(\eta_{sp}/c)/c$ curve. The assumed proportionality between intrinsic viscosity and the dimensions of the chain is true only at infinite dilution. Marked changes in $[\eta]$ with solvent involve a very drastic change in coiling of the molecule, and this is possible only with highly flexible chains. This seems to provide a fairly satisfactory qualitative picture of the behaviour of polystyrene and of the small variations of $[\eta]$ with solvent for the rigid chains of the cellulosic materials. Reported data on the flexible polyvinyl chloride molecule are inconsistent with this picture, and must have their origin in some other factors.[43]

A tendency towards solvation, which occurs when polymer/solvent interaction is preferred, promotes intermolecular contacts between separate chains as the flexible polymer chains uncurl, and this increases the slope of the $(\eta_{sp}/c)/c$ curve above that of an indifferent solvent. On the other hand, curling of the chain in a bad solvent reduces the contacts and lessens the slope of the curve. With rigid chains, modification of the shape by the solvent is relatively unimportant, but association of molecules would be greater in a poor solvent, and would give rise to an increase in viscosity. Hence, with rigid molecules the poorest solvent would give the greater slope of the $(\eta_{sp}/c)/c$ curve. The problem is undoubtedly very involved, and conclusions drawn solely from viscosity measurements must be treated with reserve unless they are combined with other observations, such as the effect of temperature on viscosity, and the dependence of molecular size (association) on temperature as determined by osmotic pressure or light scattering measurements.

## EFFECT OF TEMPERATURE ON VISCOSITY OF SOLUTIONS

The variation of viscosity of polymer solutions with temperature depends very much on the nature of the solvent. In the previous section it has been shown that the intrinsic viscosities and slopes of the $(\eta_{sp}/c)$/concentration curves are determined by the interaction energies of the polymer chains with the solvent, and thus according as solutions are formed with the evolution of heat (attraction between solvent and polymer) or with the absorption of heat. If we consider only the energetic factors, the effect of the solvent will be damped down by increase in temperature. In the former case the slope of the $(\eta_{sp}/c)/c$ curve will be decreased on raising the temperature, and in the latter it will be increased towards what Mark has termed the 'unbiased' mean value that would be observed in athermal solutions. When the heat of mixing is zero—that is, in an indifferent solvent—the viscosity relationships

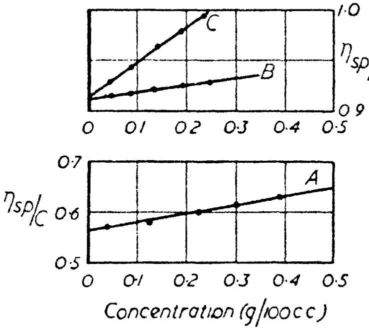

*Figure 40. Temperature dependence of viscosities of dilute solutions*

- A *polyvinyl acetate in ethyl acetate at 25°C and 50°C*
- B *polyvinyl chloride in cyclohexanone at 50°C*
- C *polyvinyl chloride in cyclohexanone at 25°C*

(*Reference:* 43)

will be unchanged by temperature. These qualitative conclusions represent, of course, over simplification, because in all cases high temperature causes increased motion of the segments, which tends to restore the flexible chain to the randomly kinked configuration and the unbiased mean.

The above effects have been observed by FRITH[43] for solutions of polyvinyl acetate and polyvinyl chloride. The former in ethyl acetate forms an athermal solution, and, as shown in *Figure 40*, the specific viscosity is independent of temperature. With a polar polymer such as polyvinyl chloride in a polar solvent, which does not give an athermal solution, increase in temperature decreases the $\eta_{sp}/c$ values, although the intercept $[\eta]$ remains the same. Similar results have been observed with this material in mixed solvents.

In hydrocarbons or chlorinated solvents the viscosity of rubber and polystyrene decreases with temperature[40] (*Table XXII*), but in mixtures containing a non-solvent the specific viscosity increases with increase in temperature, as would be expected, owing to the uncurling of the highly flexible molecule at the higher temperature.

*Table XXII*

$\eta_{sp}$ *as a Function of Temperature*[40]

| *Substance* | $\eta_{sp}$ *at* 25°*C* | $\eta_{sp}$ *at* 60°*C* |
|---|---|---|
| *Rubber in toluene* . . . . . . . | 0·390 | 0·373 |
| ,, *carbon tetrachloride* . . . . | 0·466 | 0·430 |
| ,, *toluene* + 14% *methanol* . . . | 0·205 | 0·243 |
| *Polystyrene in toluene* . . . . . . | 0·370 | 0·350 |
| ,, *toluene* + 10% *methanol* . . . | 0·320 | 0·317 |
| ,, *toluene* + 20% *methanol* . . . | 0·160 | 0·185 |
| ,, *toluene* + 10% *amyl alcohol* . . | 0·336 | 0·340 |
| ,, *toluene* + 20% *amyl alcohol* . . | 0·170 | 0·210 |

## V

## VISCOSITY AND MOLECULAR WEIGHT

The simplest and most widely used method of determining molecular weights of long chain polymers is by the measurement of the viscosity of a dilute solution. The method is not at present an absolute one, and its application therefore demands the correlation of the viscometric results with some other method of accurate determination of molecular weights. Although the theoretical and experimental basis of the law connecting viscosity with molecular weight has been widely discussed, the true form of the relationship still remains an unsettled question. The cause of the difficulty is the determination of the constants of proportionality in the equation originally proposed by Staudinger for linear molecules. This law relates the specific viscosity of a solution to the molecular weight according to

$$\eta_{sp}/c = Km \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

Whilst there is abundant experimental evidence to show that the molecular weight measured by some absolute method is proportional to $\eta_{sp}/c$ when extrapolated to infinite dilution, the simple form of the Staudinger equation is not generally applicable. Two modifications of the equation have been proposed

$$[\eta] = Km + const \quad . \quad . \quad . \quad . \quad . \quad (29)$$

and

$$[\eta] = Km^{\beta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

where $[\eta]$ is the intrinsic viscosity and $\beta$ constant. The latter equation may also require an additional constant in order to extend its application to low molecular weight polymers. It is obvious that the original Staudinger equation is the special case of equation (30) when $\beta = 1$.

Before discussing the experimental results it is necessary to explain the various units employed by different workers in expressing $\eta$ and $K$. As we have already observed on page 162, concentrations should, in theory, be expressed on a volume basis ($c_v$), but since this is often difficult experimentally, weight per unit volume (100 ml), denoted by the symbol $c$, is generally used. Staudinger and his school, on the other hand, express the concentration in base mols per litre ($c_m$), where one base mol (or *Grundmol*) is that weight of polymer in grams which is equal to the weight of the repeating unit. Thus $c_m = 1$ for a solution of polystyrene ($C_6H_5CH{=}CH_2 = 104$) containing 104 g per litre. When $c_m$ is used, the corresponding constant in the Staudinger equation is denoted by $K_m$. An equivalent form of the equation which is often met in the literature is

$$\overline{DP} = k[\eta]$$

where $\overline{DP}$ is the degree of polymerization or number of monomeric units combined in the molecule. If $[\eta]$ is expressed in the unit of grams per 100 ml, then $k = \dfrac{1}{10K_m}$.

The linear form of viscosity/molecular weight equation has been found to be obeyed for a series of condensation polymers of linear structure (polyesters) and of relatively low molecular weight. With these polymers the molecular weights necessary for the establishment of the law were determined by end group methods. BAKER, FULLER and HEISS [45] found that the relationships

$$\eta_{sp}/c = 0{\cdot}42 \times 10^{-4} m_w - 0{\cdot}03$$

or

$$\ln \eta_r/c = 0{\cdot}31 \times 10^{-4} m_w + 0{\cdot}07$$

were obeyed for fractionated ω-hydroxyundecanoic acid polymers of molecular weights from 202 to 25,000 in chloroform solution at 25°C. A linear relationship was obtained when $\eta_{sp}/c$ was plotted against the number average molecular weight. The use of the latter instead of the weight average molecular weight is permissible in this case, since the ideal distribution in this series of polymers gives a constant ratio for $\overline{m}_n/\overline{m}_w$. This was found to be 0·51 for the highest molecular weights and 0·52 for the lowest molecular weights, in close agreement with theory. Viscosity determinations on artificial mixtures established that the weight average molecular weight, rather than the number average, was measured in viscosity studies of these inhomogeneous polymers.

A similar form of relationship has been found by FLORY and STICKNEY,[46] who measured the viscosities of dilute solutions in chlorobenzene and diethyl succinate of twelve decamethylene adipates, of molecular weights ($\overline{m}_w$) in the range 1,500–30,000.

In the low molecular region MEYER and VAN DER WIJK [47] have made accurate determinations of the viscosities of the paraffinic hydrocarbons $C_{17}$ to $C_{34}$ ($m = 240$ to $478$) and find that

$$\eta_{sp}/c = 14{\cdot}55 \times 10^{-5} m - 0{\cdot}01598$$

Other polymers have been found to obey this form of the viscosity law. The additive constant is usually small, and has a value below 0·1 in all cases so far studied. Extrapolation of equation (29) to very high molecular weights shows that $\ln \eta_r/c$ would be so much greater than the constant that the latter would be negligible and the equation of Staudinger's law, $[\eta] = Km$, would hold.

Much recent work on polymers of high molecular weights has indicated that equation (30)

$$[\eta] = Km^{\beta}$$

is of general applicability in describing the viscosity/molecular weight relationship for a wide range of materials.

A detailed and complete investigation by FLORY on the solution viscosity and osmotic molecular weights of fractionated polyisobutene,[48] having molecular weights between 5,000 and 1,300,000, shows that the results can be represented accurately by equation (30), with $K = 3{\cdot}60 \times 10^{-4}$ and $\beta = 0{\cdot}64$. The variation of $[\eta]$ with molecular weight is shown in *Figure 41.* The plot of log [$\eta$] against log $m$ is linear, and the equivalent expression for Flory's results in diisobutylene at 20°C is

$$\log m = 5{\cdot}378 + 1{\cdot}56 \log [\eta]$$

*Figure 42* shows the corresponding plot of log [$\eta$] against log [$n$], where $n$ is the chain length for fractions of the polar polymer polymethyl methacrylate.[22] These results and some others to which equation (30) applies are summarized in *Table XXIII.* The value of

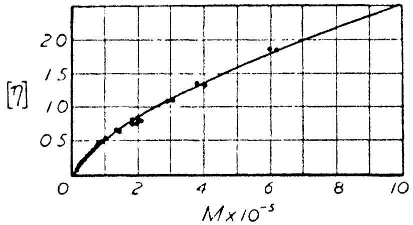

*Figure 41. Dependence of intrinsic viscosity on molecular weight for polyisobutene fractions in diisobutylene at 20°C.* $\eta = 3{\cdot}60 \times 10^{-4}$ *and* $\beta = 0{\cdot}64$.

(*Reference* : 48)

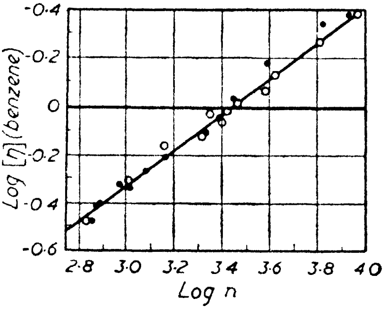

*Figure 42. Relation between chain length (determined by osmotic pressure measurements) and intrinsic viscosity for sharp fractions of polymethyl methacrylate*

$$n = 2{\cdot}81 \times 10^3[\eta]^{1{\cdot}32}$$

(*Reference* : 22)

*Table XXIII*

*Molecular Weight/Viscosity Law :* $[\eta] = Km^{\beta}$

(*Values for K and β have been established by comparing osmotic and viscosity measurements on fractionated samples*)

| *Substance* | *Solvent* | *Mol wt range* | *K* | *β* | *Authors* |
|---|---|---|---|---|---|
| *Polyisobutylene* | *Diisobutylene* | 5,000–1,300,000 | $3{\cdot}6 \times 10^{-4}$ | 0·64 | 48 |
| *Polyvinyl chloride* | *Cyclohexane* | 28,000– 102,000 | $7{\cdot}0 \times 10^{-5}$ | 1·0 | 53 |
| *Cellulose acetate* | *Acetone* | 25,000– 126,000 | $9{\cdot}1 \times 10^{-3}$ | 0·78 | 54, 58 |
| *Polymethyl methacrylate* | *Benzene* | 50,000–1,000,000 | $9{\cdot}4 \times 10^{-4}$ | 0·76 | 22 |
| *Polystyrene* | ,, | *low* | $3{\cdot}6 \times 10^{-5}$ | 1·0 | 49 |
| *Polystyrene prepared at 60°C* | *Toluene* | 550,000–2,050,000 | $1{\cdot}28 \times 10^{-4}$ | 0·70 | 50, 58 |
| *Polystyrene prepared at 120°C* | ,, | 108,000– 340,000 | $5{\cdot}5 \times 10^{-3}$ | 0·80 | ,, |
| *Polystyrene prepared at 180°C* | ,, | 169,000– 110,000 | $1{\cdot}0 \times 10^{-2}$ | 1·10 | ,, |
| *Rubber* | *Benzene* | 7,000– 350,000 | $1{\cdot}6 \times 10^{-5}$ | 0·96 | 51 |
|  | ,, | 40,000–1,500,000 | $5{\cdot}0 \times 10^{-4}$ | 0·67 | 52 |

the exponent $\beta$ is definitely not always unity as proposed by Staudinger, but depends on the nature of the polymer.

The results of ALFREY, BARTOVICS and MARK[50] on styrene show that both $K$ and $\beta$ depend on the temperature of polymerization, which they interpret as resulting from various degrees of branching of the polymer chains in the various samples. From the data in *Table XXIV* it is seen that the $\mu$ and $k'$ deduced from osmotic pressure/concentration and viscosity/concentration measurements, equations (20) and (27), although independent of molecular weight for any sample, were dependent on the temperature at which the sample was prepared. This certainly indicates a 'different internal architecture of the macromolecules' prepared at different temperatures but does not, of necessity, as pointed out by HUGGINS,[55] imply different degrees of branching. If branching occurred to a greater extent in the polymer produced at the higher temperatures, then for the same molecular weights these polymers would have a less extended form and thus a smaller $[\eta]$. This should correspond to a smaller value of $\beta$ in the viscosity/molecular weight equation, although the opposite is observed. Huggins has suggested that the chains may have different stereochemical structures which would produce differences in the average degree of coiling of the chains according to the temperature of their formation.

*Table XXIV*

*Molecular Weights, Intrinsic Viscosity, and Osmotic Pressure Constants of Polystyrenes*[38] *(wherein K is calculated from* $[\eta]_v = Km^{\beta}$ *and* $[\eta]_v$ *is the volume fraction intrinsic viscosity)*

| *Temperature of polymerization, °C* | *Molecular weight (osmotic pressure)* | $[\eta]_v$ | *Constants* |
|---|---|---|---|
| 60 | 2,050,000 | 355 | $k' = 0{\cdot}42$ |
| | 1,580,000 | 295 | $\mu = 0{\cdot}48$ |
| | 890,000 | 200 | $K = 1{\cdot}6 \times 10^{-2}$ |
| | 550,000 | 140 | $\beta = 0{\cdot}70$ |
| 120 | 344,000 | 155 | $k' = 0{\cdot}33$ |
| | 240,000 | 118 | $\mu = 0{\cdot}45$ |
| | 167,000 | 86 | $K = 6{\cdot}6 \times 10^{-3}$ |
| | 108,000 | 62 | $\beta = 0{\cdot}80$ |
| 180 | 169,000 | 73 | $k' = 0{\cdot}21$ |
| | 145,000 | 59 | $\mu = 0{\cdot}43$ |
| | 132,000 | 53 | $K = 4{\cdot}0 \times 10^{-4}$ |
| | 110,000 | 45 | $\beta = 1{\cdot}10$ |

It is not certain, therefore, whether branching is responsible for the change of the exponent. In fact, the exact meaning of the arbitrary constants $K$ and $\beta$ and their variation with structure and other factors is far from clear. Further studies on the preparation of branched polymers and methods for the determination of the degree of branching need to be developed to supplement viscosity measurements. Branching may be much more common with chain polymers than is normally supposed, and its investigation should provide a profitable field of research.

In recent investigations on cellulose acetate in acetone and cellosolve, BADGLEY and MARK[56] find that equation (30) is inadequate over a wide range of molecular weights. Deviations from the law occur for molecular weights above 100,000, and this they interpret as being due to a gradual change from a rod-like to a coiled structure, with increase in size of the molecule. They proposed a new empirical viscosity/molecular weight equation containing three empirical constants.

## MOLECULAR WEIGHT AVERAGE FROM VISCOSITY MEASUREMENTS

If Staudinger's law is assumed to be true ($[\eta] = Km$) for each component of the mixture, and we let $(\eta_r - 1)_i$ be the viscosity increment of the $i$th polymer component in the solution, then

$$(\eta_r - 1)_i = Kc_i m_i$$

but

$$\eta_r - 1 = \Sigma(\eta_r - 1)_i = K\Sigma c_i m_i$$

and

$$[\eta] = \left[\frac{\eta_r - 1}{c}\right]_{c \to 0} = \frac{K\Sigma c_i m_i}{\Sigma c_i}$$

and since $c_i$ is proportional to the weight fraction, $w_i$, of the $i$th species

$$[\eta] = \frac{K\sum_i w_i m_i}{\sum_i w_i}$$

$$= \frac{K\sum_i n_i \,.\, m_i^2}{\sum_i n_i m_i} \quad . \quad . \quad . \quad . \quad . \quad (31)$$

where $n_i$ is the number of the $i$th type molecules. Hence if Staudinger's law is obeyed (*i.e.* $\beta = 1$) the intrinsic viscosity gives the weight average molecular weight. If $\beta$ is not equal to unity and the more general relationship (30) holds, then a different average molecular weight $\overline{m}_v$, termed the viscosity average molecular weight, is obtained. By an argument identical with the above, employing equation (30) instead of equation (28), it follows that

$$[\eta] = K\left[\frac{\sum_i n_i m_i^{\beta+1}}{\sum_i n_i m_i}\right]^{1/\beta}$$

and

$$\overline{m}_v = \left[\frac{\sum_i n_i m_i^{\beta+1}}{\sum_i n_i m_i}\right]^{1/\beta}$$

This equation reduces to equation (31) when $\beta = 1$.

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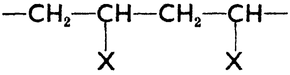
# CHAPTER 6

# THE STRUCTURE, STEREOCHEMISTRY AND CRYSTALLINITY OF HIGH POLYMERS

## I

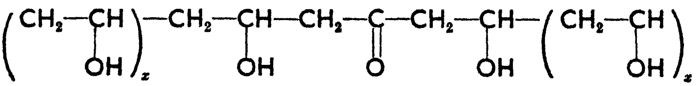
## CHEMICAL STRUCTURE OF VINYL POLYMERS

IT WAS POINTED out in Chapter 1 that the evidence obtained by the application of the orthodox methods of organic chemistry to the elucidation of the structure of long chain vinyl polymers shows that the structural units are arranged predominantly in the regular head-to-tail sequence



$$-CH_2-\underset{X}{\underset{|}{CH}}-CH_2-\underset{X}{\underset{|}{CH}}-$$

The substituent X, whether it be an atom such as chlorine, or a complex group like $COOCH_3$, occurs at alternate positions in the chain. In general, the organic methods do not rule out the possibility of a small degree of head-to-head and tail-to-tail arrangements, since such methods would not be sensitive to a small percentage of either of these arrangements or to slight branching of the chains. In order to determine the presence of these abnormal arrangements, it is necessary to supplement organic analysis by physical methods, such as absorption spectroscopy, which can be employed to detect and estimate particular types of atomic and molecular arrangements. Much scattered evidence exists which indicates unexpected chemical linkages and other than head-to-tail arrangements in chain molecules. Thus, CLARK and BLONT [1] have recently shown by a combination of spectrophotometric and chemical methods that polyvinyl alcohol contains carbonyl groups randomly distributed along the chain to the extent of about 0·4 mol per cent



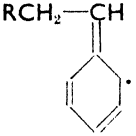
$$\left(CH_2-\underset{OH}{\underset{|}{CH}}\right)_x-CH_2-\underset{OH}{\underset{|}{CH}}-CH_2-\underset{O}{\underset{\|}{C}}-CH_2-\underset{OH}{\underset{|}{CH}}-\left(CH_2-\underset{OH}{\underset{|}{CH}}\right)_x$$

In all examples of vinyl polymers so far examined in detail, the head-to-tail arrangement is preferred. This seems to be a natural result of the growth process when this occurs through a free radical mechanism. If it is assumed that the catalyst is a source of free radicals, then the radical R may add to the monomer in either of the following ways

$$R\cdot + CH_2{=}CHX \longrightarrow \underset{\text{(I)}}{\cdot CH_2{-}CHRX} \quad . \ . \ . \quad (1)$$

$$R\cdot + CH_2{=}CHX \longrightarrow \underset{\text{(II)}}{RCH_2{-}\dot{C}HX} \quad . \ . \ . \quad (2)$$

In general, reaction (2) will be preferred because the radical $RCH_2{-}\dot{C}HX$ formed is stabilized by resonance with the substituent X to a much greater extent than radical (I). For example, if X is a phenyl group, then radical (II) has many resonance states of the type



whereas with (I) the additional resonance with the phenyl group is inhibited. Since radical (II) possesses the lower energy, the initiation process occurs preferentially by reaction (2).

In the succeeding steps, growth may occur by either reaction (3) or reaction (4)

*Head-to-tail* $RCH_2{-}\dot{C}HX + CH_2{-}CHX \longrightarrow RCH_2{-}CHX{-}CH_2{-}\dot{C}HX$ . (3)

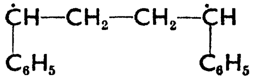
*Tail-to-tail* $RCH_2{-}\dot{C}HX + CH_2{-}CHX \longrightarrow RCH_2{-}CHX{-}CHX{-}\dot{C}H_2$ . (4)

If reaction (4) takes place, or if the initiating radical has the structure $\cdot CH_2{-}CHXR$, then the further growth process (5) may occur

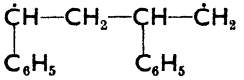
*Head-to-head* $RCHX{-}\dot{C}H_2 + CH_2{-}CHX \longrightarrow RCHX{-}CH_2{-}CH_2{-}\dot{C}HX$ . (5)

It is obvious that in the head-to-tail growth the resonance energy of the radical formed will be the same as that involved in the initiation process and no change in resonance energy is involved. This will not be so for the tail-to-tail or head-to-head growth processes (4) and (5). In reaction (4) the resonance energy of the radical formed will be less than that of the attacking radical, whereas in reaction (5) the converse is true. Thus, head-to-head addition, ignoring stereochemical factors for the present, is energetically more probable than tail-to-tail addition. However, head-to-head reaction cannot occur as a sole reaction step, but must always be followed by a tail-to-tail or tail-to-head reaction. It therefore follows that the more stable initial radical $RCH_2-\dot{C}HX$, or the radical with a terminal $CH_2-CHX\cdot$ group which would be formed after a head-to-head or head-to-tail step, grows preferentially as a head-to-tail configuration because this preserves the more stable radical ending. When the stabilizing influence of X is not very large, the rates of head-to-tail growth may not be very much greater than that of the other processes, and in such cases a small amount of head-to-head and tail-to-tail structures may be found in the polymer.

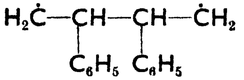
A similar conclusion may be deduced if we assume diradical initiation. Selecting the styrene radical for illustration, the growth reaction may lead to either of the following radicals



$$\begin{array}{cccccc}\dot{C}H & - & CH_2 & - & CH_2 & - & \dot{C}H\\ | & & & & & & |\\ C_6H_5 & & & & & & C_6H_5\end{array}\quad . \; . \; . \; . \; . \; . \quad \text{(III)}$$

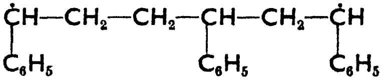


$$\begin{array}{ccccccc}\dot{C}H & - & CH_2 & - & CH & - & \dot{C}H_2\\ | & & & & | & & \\ C_6H_5 & & & & C_6H_5 & & \end{array}\quad . \; . \; . \; . \; . \; . \quad \text{(IV)}$$

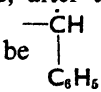


$$\begin{array}{ccccccc}H_2\dot{C} & - & CH & - & CH & - & \dot{C}H_2\\ & & | & & | & & \\ & & C_6H_5 & & C_6H_5 & & \end{array}\quad . \; . \; . \; . \; . \; . \quad \text{(V)}$$

Of these diradicals, the head-to-head form (III) is the most probable structure on account of large resonance stabilization by the terminal phenyl groups. Further growth of (III), on the radical stabilization hypothesis, would correspond to head-to-tail attachment



$$\begin{array}{ccccccccccc}\dot{C}H & - & CH_2 & - & CH_2 & - & CH & - & CH_2 & - & \dot{C}H\\ | & & & & & & | & & & & |\\ C_6H_5 & & & & & & C_6H_5 & & & & C_6H_5\end{array}$$

and succeeding processes would follow this course. The monomer addition to (III) would, on energetic grounds, be a more difficult process than addition to either (IV) or (V), since with the latter structures head-to-head attachment would correspond to a gain in stability. In each case, after the third unit had been added, the terminal group would be  $\begin{array}{c}-\dot{C}H\\ |\\ C_6H_5\end{array}$ and head-to-tail addition would be the preferred process in succeeding stages.

These generalizations may be expressed in a quantitative manner in terms of the heats of reaction.[24] In the head-to-tail addition the heat of polymerization is

$$\Delta H_1 = -D_{C=C} + D_{C-C}$$

since there is no resonance energy change on the attachment of the radical. The corresponding heat for head-to-head addition, $\Delta H_2$, is

$$\Delta H_2 = -D_{C=C} + D_{C-C} - R_i + R_f$$

where $R_i$ and $R_f$ are the resonance energies of the radical before (initial) and after (final) monomer addition. If the head-to-head attachment is followed by a tail-to-tail reaction, the heat of the latter process is

$$\Delta H_3 = -D_{C=C} + D_{C-C} + R_i - R_f$$

Hence, if head-to-tail addition is not the normal reaction course, the heat of reaction will alternate from step to step by the amount $2R_i - 2R_f$. In the above arguments we have ignored the influence of the size of the substituents in influencing the type of structure which is formed. This is only of minor importance with the mono-substituted ethylenic derivatives, but has a large influence in the polymerization of disubstituted products. A. G. Evans and M. Polanyi [2] have calculated the heats of the various reactions for isobutene, and find that the head-to-tail step is 19·5 kcal exothermic, the tail-to-tail step 27 kcal exothermic, and the head-to-head step 12 kcal per mol exothermic. The measured heat of polymerization is 12·8 kcal per mol. The chemical and x-ray evidence [3] supports a head-to-tail structure of the polymer, but on building scale models of the possible structures,[2] it is found that in the head-to-tail structure steric hindrance between the methyl groups is so great that in order to build a molecule at all, successive isobutene units have to be rotated with respect to each other, so that the methyl group of one isobutene fits in between the two methyl groups of the next isobutene unit. In this way, the molecule assumes a spiral configuration in keeping with the structure deduced from x-ray investigations. When the polyisobutene model is constructed according to the head-to-head, or tail-to-tail structure, no steric hindrance is observed. It may therefore be assumed that steric influences in the formation of the head-to-tail arrangement cause the heat of polymerization to be some 7 kcal less than expected in the absence of steric hindrance. With no steric effect the radical mechanism would result in head-to-tail addition, but the presence of the steric effect in the addition reaction reduces its exothermicity, and brings it close to that of the head-to-head step. This makes head-to-head, tail-to-tail types of addition possible, as well as the head-to-tail type. If both occur we should expect the chain to consist of a more or less random arrangement of the linkages. This is not in agreement with the very highly crystalline nature of the stretched polymer, and it appears that, in spite of the steric effect, the head-to-tail configuration is preferred. Polymethyl methacrylate, like isobutene, is a 1 : 1′-disubstituted ethylene, and should show large steric effects. The measured heats of the polymerization of methyl methacrylate and of acrylic acid are 11·6 kcal and 18·3 kcal respectively. Assuming head-to-tail type reaction, it seems reasonable to attribute this difference to steric factors.

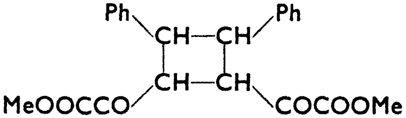
The calculated heat of polymerization of gaseous isoprene[2] to a sterically unstrained rubber is 18·7 kcal per mol. The experimental value is 17·9 kcal per mol.[4] The agreement between the values confirms the expected absence of steric hindrance in the polymer molecule.

In general, scale models of the monosubstituted ethylenes show that the polymer molecule is free of steric hindrance. In these cases the heat of polymerization should be normal.

It is well established that structural factors have an important influence on the tendency of polymerization and copolymerization (Chapter 1). The steric hindrance in the propagation step is the most logical explanation of the fact that monomers, in which a hydrogen atom on each of the carbon atoms of the double bonds is substituted (except by fluorine), do not undergo polymerization. The relative stabilities of the radicals may also be an important consideration. Simple olefinic molecules which do not form long chain polymers may be subdivided broadly into two classes: *a* those which dimerize readily, *b* those which do not polymerize or even dimerize. Most of these molecules have the structure $\mathrm{XCH{=}CHY}$. The former group includes stilbene, allene and its derivatives, ketenes, methylbenzal pyruvate, benzylidene acetophenone, acenaphthylene, and the latter maleic and fumaric acids, crotonic acid, and benzoyl acrylic esters. For example, methylbenzal pyruvate (VI), when activated photochemically in benzene solution, forms a dimer (VII) which was shown to be a derivative of truxinic acid:

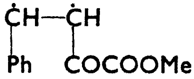
$\mathrm{PhCH{=}CHCOCOOMe}$

(VI)



(VII)

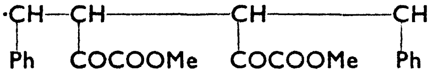
Postulating that the photoinitiating mechanism is the opening of the double bond, to form the free radical (VIII)



$$\underset{\mathrm{Ph}}{\dot{\mathrm{C}}\mathrm{H}}-\underset{\mathrm{COCOOMe}}{\dot{\mathrm{C}}\mathrm{H}}$$

(VIII)

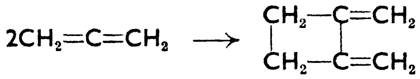
this will be highly stabilized at both ends, on account of resonance with the phenyl and COCOOMe groups. The addition of a monomer molecule yields three possible types of diradical, the most probable of which would be the one with the phenyl groups at the end of the chain



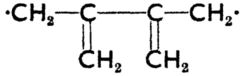
$$\cdot\underset{Ph}{CH}-\underset{COCOOMe}{CH}-\underset{COCOOMe}{CH}-\underset{Ph}{CH}\cdot \qquad (IX)$$

The resonance stabilization of this structure is so great that it shows little tendency to react with monomer molecules, and the two ends of the radical react to form a four-membered ring. An alternative explanation of the dimerization is that no intermediate diradical is formed, but that (VIII) reacts directly with a monomer molecule to form (VII), and polymerization is inhibited purely on steric grounds.

Another example of enhanced resonance in which steric influences seem to be absent is that of allene, $CH_2{=}C{=}CH_2$, and its derivatives, which on heating to 140°C form cyclobutane derivatives



If the thermal reaction is the opening of the double bond, then the diradical produced on monomer addition



$$\cdot CH_2-\underset{\overset{\|}{CH_2}}{C}-\underset{\overset{\|}{CH_2}}{C}-CH_2\cdot$$

will possess several equivalent structures, and the structure will be so stabilized that ring formation will be preferred to chain growth.

Numerous olefins of the structure $XCH{=}CHY$ do not dimerize or polymerize on thermal or photoactivation, but undergo a *cis–trans* isomerization; for example, maleic and fumaric acids and esters, benzoylacrylic esters ($C_6H_5COCH{=}CH{-}COOCH_3$). The existence of the isomeric change indicates that the double bond has been sufficiently activated to permit free rotation, and the explanation of the non-polymerizability is a result of *a* the stability of the diradical, $X{-}\dot{C}H{-}\dot{C}H{-}Y$, and *b* the steric hindrance in the propagation reaction.

It is of interest in this connection to note that substances such as maleic anhydride and stilbene, which when alone do not polymerize, readily produce a copolymer with vinyl monomers. Furthermore, the above pair of non-polymerizable monomers copolymerize together. Since the activity of the radical formed from the maleic derivative is such that it does not add its own kind of monomer, it is necessary, for instance, in the polymerization of diethyl maleate with styrene, to postulate that a styrene monomer always adds to a maleate radical. The styrene radical so formed may add on a maleate monomer. Therefore, the copolymer cannot consist structurally of more than 50 per cent of the maleate residues. There is no such restriction on the styrene content, which may readily form sequences of styrene units in the copolymer, as in polystyrene.

# II

# PHYSICAL METHODS OF DETERMINING STRUCTURE

## INFRA-RED ABSORPTION SPECTRA

In recent years the measurement of their infra-red absorption spectra has become a most powerful tool for the study of the internal molecular structure and physical behaviour of macromolecules. The contributions which infra-red absorption measurements have made to our knowledge of *a* the structure of molecules (*e.g.* water, ammonia), *b* the nature and origin of interatomic forces (*e.g.* the hydrogen bond), and *c* analysis and identification of molecules, are well known. The recent rapid progress in extending the field to more complex systems is mainly a direct result of the improvements in technique which have made possible the rapid recording of infra-red spectra, and have thus enabled the building up of the necessary fundamental background information.

The infra-red absorption spectrum of a substance consists essentially of bands which correspond to the characteristic vibrational frequencies of the molecule as a whole or of particular groupings within it. Theoretically, the infra-red spectrum of a molecule is a unique ‘fingerprint’ which cannot be duplicated by any other molecule. Although the molecule vibrates as a whole, it happens that in some of the vibrations the different linkages or groupings are excited with different intensities and in fact, as has been established for some time, each given grouping of the atoms appears in absorption as a vibration frequency characteristic of the particular atomic grouping. Thus, the linkages C—H, O—H, and N—H retain their individuality in different compounds and give rise to frequencies which are only slightly affected by the rest of the molecule; others such as C=C and C=O give a fairly constant frequency in different compounds, but their exact values are rather more influenced by their environment in the molecule and by varying electronic influences. Thus, the position of the absorption band of the carbonyl group indicates whether it forms part of an acid, aldehyde, ketone, anhydride, or ester. This information has been arrived at by the study of a large number of pure compounds, and it is from a catalogue of this type of result that it is possible to infer, from small changes in the frequency of any particular grouping, the exact nature of the group.[5]

The absorption spectra of a large number of macromolecules, usually in the form of thin films, have been measured, and the application of empirical knowledge of the above type has been used for *a* the elucidation of the structure of the polymer units and their arrangement in given states of aggregation, *b* the investigation of physical or chemical processes such as plasticization or vulcanization and *c* analysis of mixtures of macromolecules. Many recent summaries of these advances in the field of high polymers have been published,[6] and in the remainder of this section we shall refer only to a few of these applications.

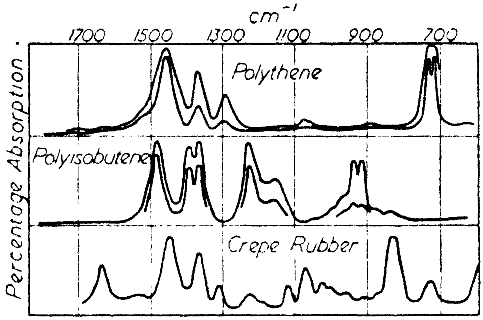
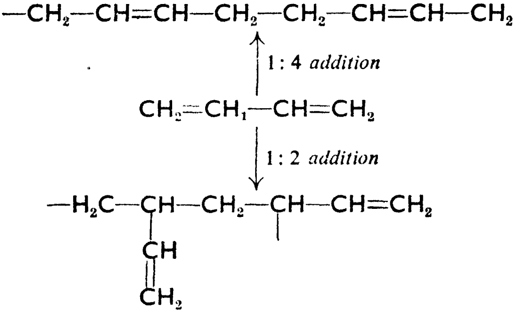


*Figure 43. Infra-red absorption of hydrocarbon polymers*
*Band at* 1,460 *cm*$^{-1}$ *due to deformation vibrations of* $CH_2$ *groups*
*Band at* 1,370–1,400 *cm*$^{-1}$ *due to deformation vibration of methyl groups*
*Band at* 725 *cm*$^{-1}$ *due to deformation vibration of* C–C *chain*
(*Reference* : 6)

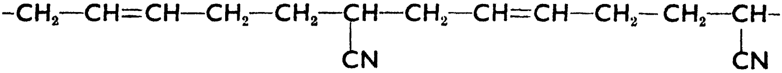
The presence in macromolecules of unexpected groups has been revealed by their absorption spectra. It is usually assumed that polyethylene consists of a perfectly straight chain of —$CH_2$— groups. Careful measurements of the intensity of absorption of polyethylene films and calibration against reference spectra of branched chain paraffins have shown that polyethylene made by high temperature polymerization contains about one methyl group per fifty methylene groups. The spectrum also indicates the presence of the >CO grouping in the chain which could result from oxidation during the polymerization.[7ab] The method is extremely sensitive for the determination of carbonyl groups, which may be estimated down to 0·01 per cent.

In the catalysed polymerization of a diene, either 1 : 2 or 1 : 4 addition may take place as, for example,



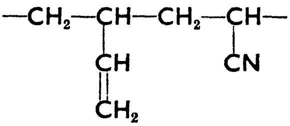
The presence of various types of olefinic linkage may be differentiated spectroscopically. The relative proportions of the above types of grouping present in butadiene polymers made by different processes have been determined in this manner.[7b]

The same method may be applied to the determination of the proportion of 1 : 2 or 1 : 4 addition in copolymerizations such as the copolymer between butadiene and acrylonitrile. This polymer may have the following chain structures, which would show either a strong band characteristic of the $R_1CH{=}CHR_2$ grouping (where $R_1$ and $R_2$ are alkyl groups) at 965 cm$^{-1}$



$$-CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}\underset{\displaystyle CN}{\underset{|}{C}H}{-}CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}\underset{\displaystyle CN}{\underset{|}{C}H}-$$

or with remaining pendant vinyl groups giving rise to bands at 909 and 990 cm$^{-1}$



$$-CH_2{-}\underset{\underset{\displaystyle CH_2}{\|}}{\underset{\displaystyle CH}{\underset{|}{C}H}}{-}CH_2{-}\underset{\displaystyle CN}{\underset{|}{C}H}-$$

Thompson and Torkington [8] showed that the bulk of the reaction occurred by 1 : 4 addition. Exactly similar considerations have been applied to the copolymer between butadiene and styrene,[10] and the polymerization of isoprene.[11]

Other features of copolymerization have been studied in this way, such as the determination of the relative amounts of the components combined in the polymer. With the butadiene/styrene copolymer, the total phenyl groups can be estimated by absorption at 760 $cm^{-1}$, and with butadiene/acrylonitrile polymers, the cyanide group from the band at about 2,250 $cm^{-1}$. Many other interesting applications could be given, such as the elucidation of the groupings in phenol- or cresol-formaldehyde resins, in the polyesters and in polyester amides, the residual hydroxyl groups and the extent of hydrogen bonding in the substituted celluloses, and the changes produced in rubber by vulcanization.[5] The results support and supplement those obtained by chemical methods, but it is evident that absorption spectroscopy, with the accumulation of more fundamental data, will help to clear up many outstanding and still unsolved problems in polymer chemistry.

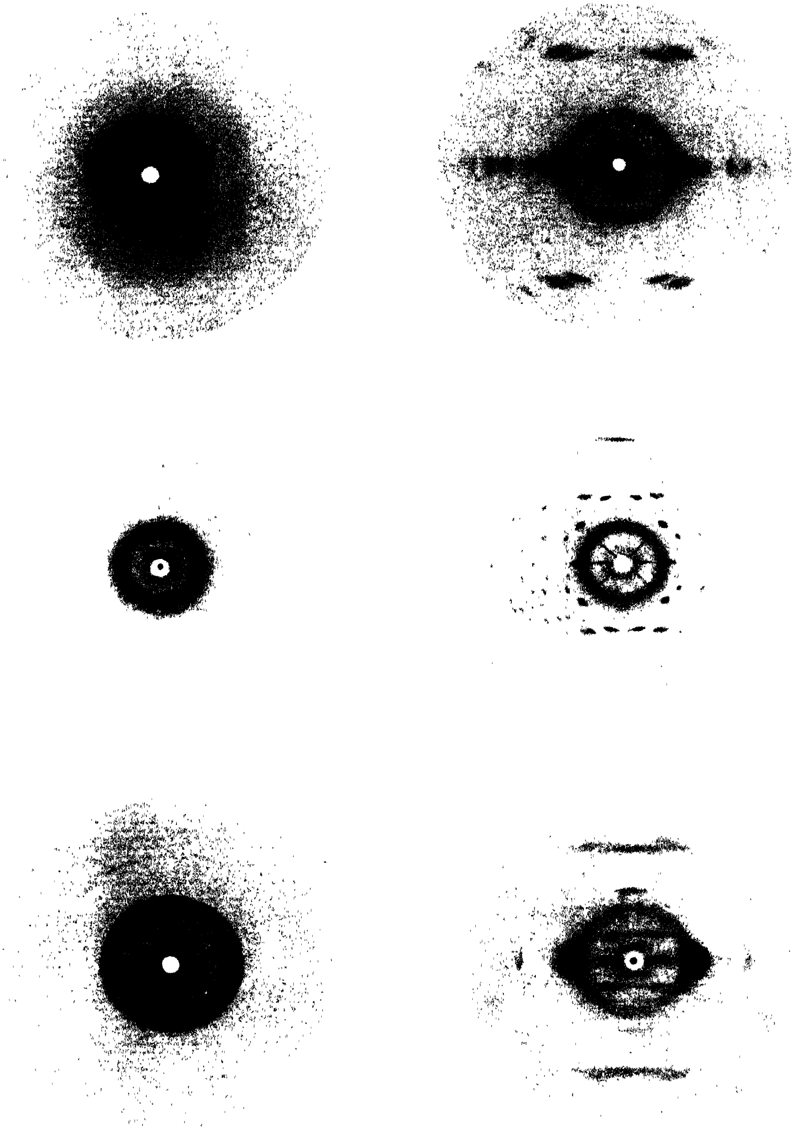
## X-RAY ANALYSIS OF POLYMERS[12]

The application of x-rays to the study of solids falls broadly into two categories: first, the study of the shape, properties, and arrangement of the atoms or molecules within a crystal, and secondly, the form, arrangement, and properties of the crystalline aggregates in a polycrystalline material. The ultimate object of the first type of investigation is the assignment of the exact position of the atoms in the crystal lattice, and even with simple substances which give high quality single crystals the analysis is often extremely difficult. In the case of high polymeric molecules which cannot be produced as single crystals, the investigation is limited to the polycrystalline, mesomorphic, or amorphous forms, and as a consequence the results are less definite and more difficult to interpret than for single substances. In a very few cases only has it yet been possible to specify completely the detailed molecular configuration and arrangement of the atoms in the high polymer. The x-ray measurements, together with chemical and other evidence for those high polymers which exist in the crystalline form, have, however, furnished useful stereochemical data which have formed a basis for the correlation of the molecular structure of the molecules with their physical and mechanical properties. In addition to the fundamental study of molecular structure, there are other important applications of the x-ray method which belong to the second category mentioned above; for instance, the study of the ratio of crystalline and amorphous materials present and the effect of variables, such as deformation, thereon, or the size and orientation of the crystals in the polymer. The importance of the latter type of measurement will be considered in the next chapter, and this section will deal primarily with the structure and stereochemistry of high polymers.

If a beam of monochromatic x-rays passes through a powdered crystalline solid, which is rotated backwards and forwards through a finite angle in order to ensure random orientation of the crystals in the specimen, rays reflected at any particular type of crystalline plane form a cone around the incident beam and appear as a ring or an arc on a photographic film placed behind the specimen at right angles to the beam. Each crystalline species produces its own well defined pattern of rings or arcs, *Plate 1*. With amorphous materials the rings are very diffuse, and not sharp, as they are with crystalline bodies. The fairly sharp diffraction rings given by polyethylene or a polyamide is evidence, therefore, that the molecules are precisely arranged, and such polymers are usually referred to as ' crystalline '. However, in almost all instances, the x-ray picture shows, in addition to the sharp rings, diffuse rings indicating the presence of disarranged molecules, and hence the material is not truly crystalline in the sense in which we use the term in referring to a single crystal of a pure chemical.

Many naturally occurring polymers such as cellulose, or certain of the proteins, exist in the form of fibres in which the small crystalline regions (crystallites) are arranged with one axis parallel, or at a fixed angle, to the axis of the fibre. Synthetic polymers such as the polyesters, polyamides, and polyethylene may be drawn out or stretched to form similarly orientated fibres. The x-ray diagram of these fibrous materials, obtained by irradiating at right angles to the fibre axis, is similar to the rotation photograph of a single crystal, since all orientations at right angles to the fibre axis are present, but instead of complete rings, the pattern appears as an array of spots. The spots are broad because the crystalline arrangement is not perfect, and they are somewhat elongated into arcs because of imperfect orientation. The spots fall on ' layer ' lines which are parallel to the fibre axis. From the layer line separation, the fibre period—that is, the identity period corresponding to the repetition of the basic pattern of the atoms along the fibre axis—can be determined unequivocally. It is from this type of photograph that much of our information on the inner structure of the polymeric substances is obtained.

A crystal is a regular assembly of some fundamental repeat unit—called the ' unit cell '. This unit pattern is a box bounded by three pairs of parallel sides, and it is the function of the x-ray



(Courtesy of W. T. Astbury)

*X-Ray Diffraction Photographs of Polymers*

*Disorientated Polythene*

*Unstretched Polyisobutylene*

*Polymethyl methacrylate*

*Polythene Fibre*

*Polyisobutylene Stretched 1,400%*

*Nylon*

crystallographer to determine the shape and dimensions of the box (unit cell)—namely, the lengths of the three sides (axes) and the angles between them. The unit cell dimensions can be deduced from an X-ray fibre photograph, but this information does not, by itself, lead to a knowledge of molecular shape. However, from a knowledge of the chemical structure, together with data on interatomic distances and crystallographic evidence of the manner of packing, the position of the atoms may be found by trial. The complete determination of the structure can be made only by the use of the intensities of the X-ray reflections. This results from the fact that, whereas the directions of the diffracted beams depend on the repeat distance within the crystal (unit cell dimensions), the intensities of the diffracted beams depend on the position of the atoms in the unit cell. The detailed interpretation of the patterns in terms of molecular configuration and arrangement is extremely difficult and not always possible, even when the chemical structure is thoroughly established. As a consequence, very few polymer structures have been worked out in detail. Some of the results obtained from X-ray studies of polymers will now be summarized.

## III
## CRYSTAL STRUCTURE OF CHAIN POLYMERS

*Vinyl Polymers*—In drawn fibres of polymers of regular structure the molecules lie approximately parallel to the fibre axis, and the unit cell dimension obtained from the layer line spacing is also the identity period of the molecule itself. In such cases measurement of the identity period may give directly the information as to the geometry of the chain and of the whole molecule, including side substituents. Thus, Bunn[13] found that the repeat distance of 2·53 Å. measured with cold drawn polyethylene threads is just the repeat distance of a fully extended zigzag chain of carbon atoms of interatomic distance C—C = 1·54 Å and carbon/hydrogen bond angle in $CH_2$ approximately 110°. It appears therefore that the chain in polyethylene has the configuration shown in *Figure 44*, which is precisely that found in the lower paraffin waxes. This was subsequently confirmed by Bunn[13] in the

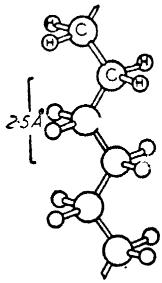


*Figure 44. Structure of molecule of polyethylene*

complete interpretation of the diffraction pattern. The arrangement is very favourable from the point of view of fitting into a crystal lattice, the nearest approach of atoms belonging to different chains being 4·3 Å. Polyvinyl alcohol [14] has the same repeat period as polyethylene, and thus its chain has also the fully extended zigzag configuration; moreover, all the hydroxyl groups must occupy corresponding stereo-positions, either all above or all below the plane of the zigzag (which is the plane of the paper in *Figure 45*). For if the hydroxyl groups were, for instance, alternately on each side of the zigzag, the repeat distance would be 2 × 2·54 Å. Polyvinyl chloride does not crystallize very well, and gives very diffuse diagrams. The repeat distance of approximately 5·1 Å is about twice that of polyvinyl alcohol, and it is probable that the chlorine atoms are alternately on each side of the plane of the carbon chain as shown in *Figure 46*. The reason for its poor crystallization is not clear, and different explanations, all concerned with the chemical non-uniformity of the structure—*i.e.* some head-to-head groups, or some chain branching during the polymerization—have been offered.

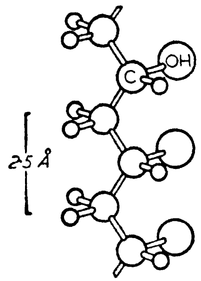


*Figure 45. Structure of molecule of polyvinyl alcohol*

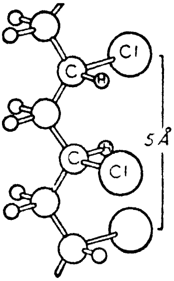


*Figure 46. Structure of molecule of polyvinyl chloride*

Polystyrene and polyvinyl acetate do not crystallize on stretching, and the X-ray patterns show only slight orientation. In polyvinylidene chloride, in which the alternate carbon atoms carry a pair of chlorine atoms, the period is 4·7 Å, rather less than the 5·06 Å for the fully extended, double zigzag chain. In terms of the head-to-tail structure this indicates a greater periodic distortion of the carbon backbone than the flat zigzag would permit in order to allow more room for the chlorine atom pairs. FULLER'S [15] interpretation of this shortening is that the pairs of chlorine atoms are turned first a little to one side and then back again, so that instead of abutting directly, they fit into one another as shown in *Figure 47*.

When the chlorine atoms in polyvinylidene chloride are replaced by pairs of methyl groups to form the rubber-polyisobutylene, the unstretched form shows a typical amorphous pattern, but in the stretched state the rubber (*Plate 1*) gives one of the best defined fibre patterns known in X-ray analysis. In the unstretched state the chains undoubtedly coil up in an irregular manner, in order to allow the methyl groups as much room as possible. The stretched state corresponds to a fibre pattern of 18·64 Å which comprises eight repeat units,[16] but is considerably less than 8 × 2·53 Å necessary for the flat zigzag chain. It is immediately apparent, from a model of this chain, that the configuration will be strongly influenced by repulsion between the methyl groups. Calculations show that methyl groups in neighbouring units require to be 3·5–4 Å apart, but if the backbone were a flat zigzag they would be only 2·53 Å apart. The situation, as may be shown by a model, is not helped by buckling the backbone, and no configuration can be constructed which will permit the methyl groups to be more than 3 Å apart. The methyl groups are therefore forced together, and this steric hindrance effect is apparent in the heat of polymerization (p. 183), which is 7 kcal/mol smaller than the value expected in the absence of steric hindrance. FULLER, FROSCH, and PAPE[16] suggested that rotation around single bonds occurs, so that the pairs of methyl groups forms a helix around the chain axis. The helix, which repeats every eight monomer units, has the correct identity period. BUNN,[17] and ASTBURY,[18] however, do not agree with these conclusions, and have proposed independently other models based on rotation of the units, giving a new spiral form, while at the same time maintaining the identity period of 18·64 Å. The test of these configurations must await a full examination of the intensities of the X-ray reflections.

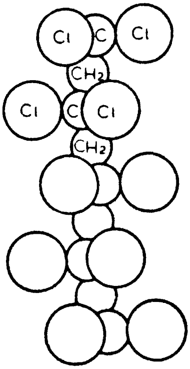
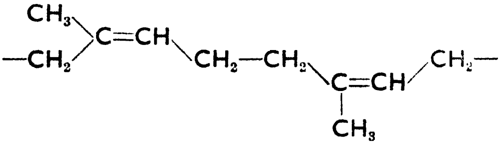


*Figure 47. Suggested chain configuration for polyvinylidene chloride* (*Reference*: 15)

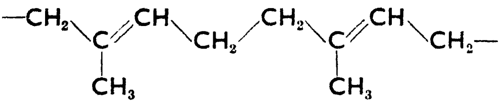
*Rubber*—Many other examples are known in which the chains do not show maximum extension, and it is clear from the previous example that the repeat distance alone is not sufficient information for determination of the configuration, and that a detailed interpretation of the entire diffraction pattern is most probably necessary for the complete stereochemical interpretation of the structure. In this respect BUNN[19] has made a considerable advance in the crystal analysis of rubber, gutta percha, and the synthetic rubber-chloroprene. Rubber and gutta percha are polymers of isoprene, $CH_2{=}C(CH_3){-}CH{=}CH_2$, in which the isoprene units are linked end to end, 1 : 4

$$—CH_2—C(CH_3){=}CH—CH_2—CH_2—C(CH_3){=}CH—CH_2—$$

and yet they have very different mechanical properties at room temperature. Furthermore, gutta percha exists in two forms (α and β) which are both different from, and not convertible to, rubber. As was originally suggested by MEYER and MARK[20] and has since been fully established, rubber and gutta percha forms are *cis* and *trans* isomers which arise from the presence of the double bond. Rubber is the *cis* form with chain bonds on the same side of the double bond, while gutta percha is the *trans* form with chain bonds on opposite sides of the double bond



*cis*



*trans*

The relationship between structure and properties may, therefore, most probably be found in the stereochemistry of the molecule. The crystal structure of these molecules has been deduced by X-ray analysis, and although the complexity of the problem does not permit of finality of structure, the results have provided a valuable guide in the interpretation of their physical properties.

The detailed structure of a single molecule of rubber proposed by Bunn is shown in *Figure 48*. A feature of great significance is the non-planar nature of the molecule, the $CH_2—CH_2$ chain lying out of the plane of the double bond unit. In order to explain the observed X-ray intensities, it is assumed that the two isoprene units which make up the geometrical units are considerably different from each other in the position of their $CH_2—CH_2$ bonds. How genuine these features are remains to be seen.

In the corresponding structure for β gutta percha proposed by Bunn, the chain, as with rubber, is pronouncedly non-planar—the $C—CH_3$ bond lying 24° out of the plane of the rest of the double bond group. JEFFREY,[21] however, has provided a model which differs significantly from that of Bunn, although it accounts equally well for the x-ray intensities. In this model (*Figure 49*) there is no distortion of the $CH_3$ group out of the plane and the $CH_2$—$CH_2$ bond is orientated 80° to the plane of the double bond instead of the 63° proposed by Bunn.

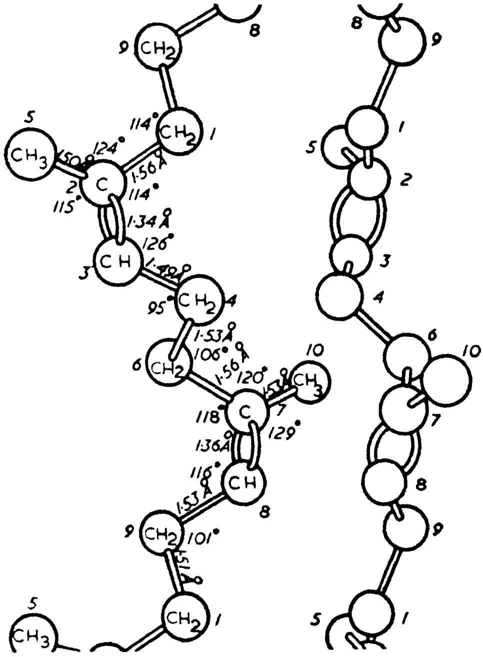


*Figure 48. Left handed rubber molecule, seen from two different viewpoints (Reference : 19)*

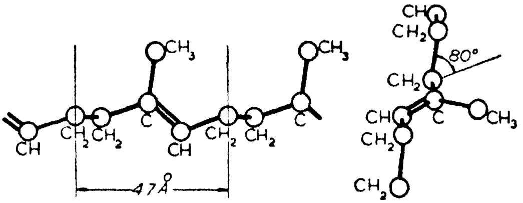


*Figure 49. Molecular structure of β-gutta percha (Reference : 21)*

*Polyesters and Polyamides*—The polyesters and polyamides, on cold drawing, form highly orientated fibres which give good x-ray fibre patterns. The extensive study of these molecules by FULLER and BAKER and their collaborators[22] constitutes one of the most important contributions in the field of the stereochemistry of long chain molecules. The ethylene polyesters of adipic, suberic, azelaic, and sebacic acids (made by the condensation of ethylene glycol with the corresponding acid) and the self polyester of ω-hydroxydecanoic acid conform essentially to the planar zigzag type of chain structure in which the chains lie along the fibre axis. A comparison of the fibre periods calculated on the basis of the zigzag chain as in polyethylene are summarized in *Table XXV*. The slight shortening of the chain may be due to a small deviation from the planar configuration or to a deviation in the oxygen bond angle.

*Table XXV*

*Fibre Patterns of the Polyesters*

| *Polyester* | *Repeating unit* | *I obs* | *I calc* |
|---|---|---|---|
| *Polyethylene adipate* | $-O(CH_2)_2OCO(CH_2)_4CO-$ | 11·71 Å | 12·21 Å |
| *Polyethylene sebacate* | $-O(CH_2)_2OCO(CH_2)_8CO-$ | 16·83 | 17·24 |
| *Polyethylene suberate* | $-O(CH_2)_2OCO(CH_2)_6CO-$ | 14·1 | 14·73 |
| *Polyethylene azelate* | $-O(CH_2)_2OCO(CH_2)_7O-$ | 31·5 | 32·0 |
| *Poly ω-hydroxyundecanoate* | $-O(CH_2)_{10}CO-$ | 27·1 | 27·3 |

The x-ray measurements also show a striking resemblance to those of the long chain paraffins, and it is evident that the same type of packing is present in all these compounds. The odd polyesters conform to the same unit cell as the hydrocarbon $C_{29}H_{60}$,

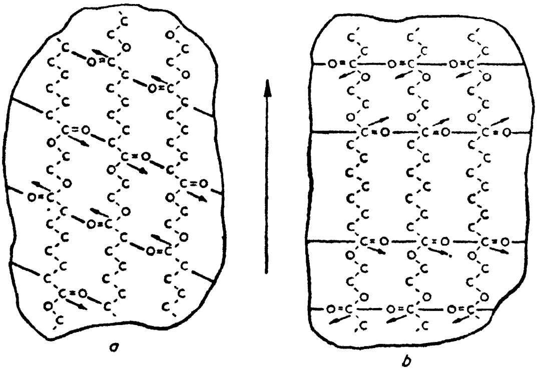
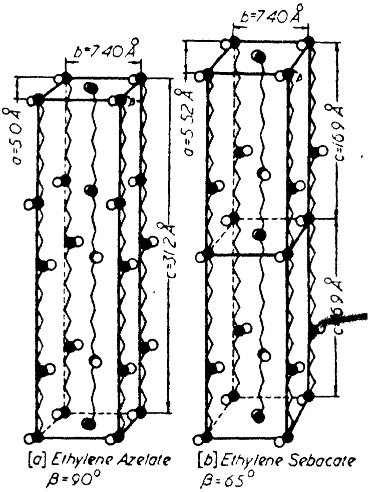


***Figure 50.** Schematic association of dipoles in dibasic acid/glycol a, even; b, odd polyesters*

*(Reference: 22b)*

except for the repeat distance. The x-ray pattern is very similar to that of polyethylene, except that there are now additional layer line reflections arising from the planes of atoms which include the oxygen. The fibre patterns [23] indicate that for the odd esters the ends of the repeating units of adjacent chains are arranged in planes perpendicular to the fibre axis. These planes are represented by the horizontal lines of *Figure 50b.* In the case of the polyesters containing an even number of carbon atoms the reflections are accounted for if the carbon atoms in the chains fall into horizontal planes and the corresponding C=O groups of succeeding chains are displaced along the chain direction with respect to one another so as to fall into planes which are inclined to the fibre direction. This structure is depicted in *Figure 50a.* The behaviour is strictly analogous to that observed in low molecular weight paraffinic esters ($C_{12}$—$C_{30}$), where, however, the chains are regarded as tilted to the polar layers, instead of the reverse, as in the present case. The phenomenon of layering of the polar groups in fibres is quite general, and of great importance in connection with their physical properties.

The even polyesters of the above series have only one chemical unit in the geometrical unit, whereas when there is an odd number of carbon atoms in the chain the fibre diagrams indicate that there are two chemical units in the geometrical unit. The possible unit cells for typical members of these series are shown in *Figure 51.*



[a] Ethylene Azelate β=90°

[b] Ethylene Sebacate β=65°

● Carbon ○ Oxygen

*Figure 51. Possible structures of polyesters suggested by Fuller: [a], odd type; [b], even type. Hydrogen atoms are omitted (Reference: 22a)*

If we go to polyester series other than ethylene, by changing from ethylene glycol to higher glycols, new phenomena are encountered. Thus, in the trimethylene glycol series the repeat distances along the fibre axis are shorter than the length of two fully extended zigzag chains by an almost constant amount of 2·8 Å. Without going into details, it has been suggested by FULLER and BAKER [22b] that this is due to a uniform folding of the chains. This results in a tilting of the chemical repeating units about the fibre axis at an average angle of 30° to it. One possible configuration is shown schematically in *Figure 52*. In this way it is possible to account for the observed shortening, as well as for the diffraction pattern. Many other polymers show this chain folding, which is probably determined by the ease of rotation around the chain bonds, and by the intermolecular forces between the chains.

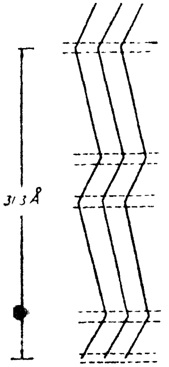


*Figure 52. Possible diagrammatic form of chain folding along fibre axis of polytrimethylene sebacate (Reference : 22b)*

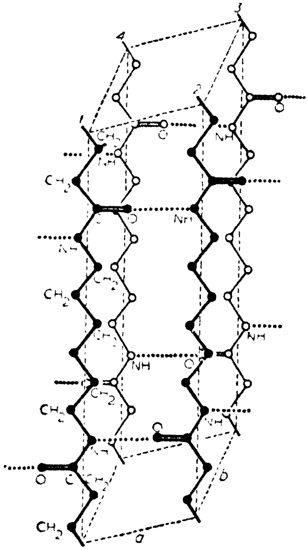
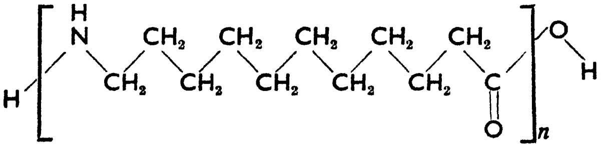
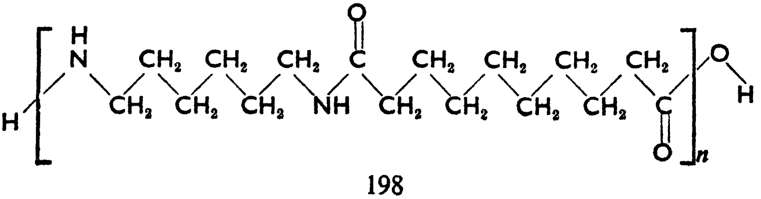


*Figure 53. Molecular structure of polyhexamethylene diamine (Nylon 66) (Reference : 26)*

The polyamides, which may be looked upon as products obtained by substituting the chain oxygen atoms of the polyesters by NH, would be expected to show similar structures to the esters, and this is generally the case. Thus, with the poly ω-undecanamide



and polyhexamethylene sebacamide



the fibre periods correspond essentially to fully extended zigzag chains.[25] In addition, the polar amide linkages form vertical and tilted dipole layers, just as was observed above in the case of the esters. The change to the polyamide structure, however, produces new effects of primary importance, due to the fact that the adjacent NH and C=O groups in neighbouring molecules form hydrogen bonds with one another. This has a pronounced effect on the properties of the polyamides, as is described in the next chapter. Recently, BUNN and GARNER [26] have carried out a detailed interpretation of the diffraction patterns of two polyamides (polyhexamethylene adipamide and sebacamide) and have found strong evidence for hydrogen bonds. The oxygen atom of one molecule and the nitrogen atom of the next are found to be in the same plane at a separation of 2·8 Å, which is characteristic of the hydrogen bond distance observed in other systems. The hydrogen bonds do not link the molecules three-dimensionally, but only in sheets, as shown in *Figure 53*. The links between the sheets are much weaker, and this influences the types of orientation taken up in the cold drawing of fibres.

# IV

# CRYSTALLINITY

X-Ray studies have shown that, although many of the linear high polymers exist in a highly crystalline state, the materials are not completely crystalline, but contain a portion of molecules which are disorientated. Other polymers, such as polystyrene, polymethacrylate, or rubber, in their normal states are shown by x-ray methods to be highly amorphous structures. Evidence has accumulated showing that many of these supposedly amorphous polymers may be transformed, under suitable treatment, into a state in which they display the properties associated with crystalline materials such as melting or optical double refraction. For instance, high molecular weight polyisobutene or rubber, on stretching, forms a highly orientated state and shows x-ray diffraction patterns and other properties common to truly crystalline materials. This change of phase from the crystalline to the amorphous and *vice versa* is of extreme importance with regard to the physical and mechanical properties of high polymers.

Chain polymers, in general, have a two-phase structure of rather complex character. Certain regions of a specimen exhibit a high degree of internal geometrical order, and are usually referred to as crystallites. These regions are unlike true crystals, in that they do not have any well defined geometric shape or boundaries characterized by the sharp edges of crystals. Actually, we can picture them as zones in which the polymeric molecules are arranged in an orderly three-dimensional arrangement of ill defined size and shape. In the amorphous or disordered regions the molecules are packed in a less orderly manner, and, for reasons which we shall consider more closely later, various factors prevent these molecules from attaining the true equilibrium configuration of the crystalline state. The amorphous and crystalline regions are not mechanically separable phases, but the same molecule (chain) may at the same time have part of its length in a crystalline, and the remainder in an amorphous, region. In fact, the same chain may pass through more than one region in which the molecules are highly orientated to regions in which disorder is predominant. This may be represented diagrammatically as shown in *Figure 54*. This idea is strongly supported by measurements of the approximate size of the crystalline zone in chain polymers and by other physical measurements to be described later. It has thus become common to define a crystalline/amorphous ratio in referring to the state of aggregation of high polymers. It must, however, be clearly understood that such a differentiation is not sharp, but that crystalline and amorphous regions of all sizes are present and that we have to regard the system as a whole as existing in states of various degrees of order or disorder.

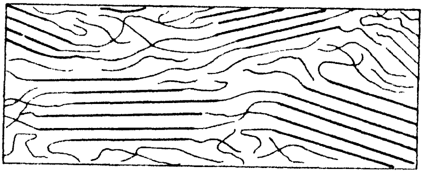


*Figure 54. Arrangement of chain molecules in ' crystalline ' polymer. Heavy lines represent crystalline regions. Chains pass through crystalline and amorphous regions*

*Crystalline/Amorphous Ratio*—Polyethylene, in common with some of the vinyl polymers, polyesters, and polyamides, is partly crystalline at room temperature. Increase in temperature causes the growth of the amorphous regions at the expense of the crystalline, until a temperature is reached at which the material is completely amorphous and is indistinguishable from a viscous liquid. This change of phase is accompanied by a change in a number of properties. These properties may be used to study melting and crystallization and they enable the calculation of the relative proportions of crystalline and amorphous phases to be made at any temperature. The most convenient properties to measure are those of specific volume and specific heat. The results obtained with polyethylene[27] are shown in *Figures 55* and *56*. If $w_x$ is the weight fraction in the crystalline form, then the observed specific volume is given by

$$[V_{obs}] = w_x[V_{cryst}] + (1 - w_x)[V_{amor}]$$

$[V_{cryst}]$ and $[V_{amor}]$ may be estimated from x-ray measurements and the linear extrapolation of the curve above the m.p in *Figure 55*. The results (*Table XXVI*) show the following dependence of the crystalline fraction on temperature.

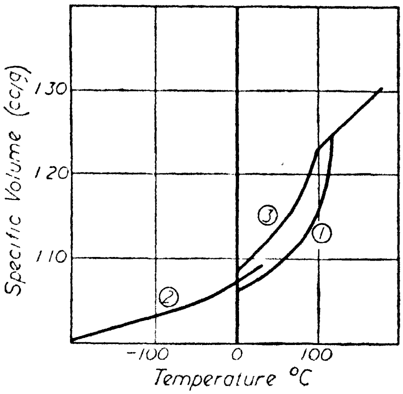


*Figure 55. Specific volume of polyethylene. The curves refer to samples of different average molecular weights*
(*Reference* : 27)

*Table XXVI*

| *Temperature* . | 0 | 20 | 40 | 60 | 80 | 90 | 100 | 105 | 110 |
|---|---|---|---|---|---|---|---|---|---|
| *% Wt crystalline* . | 55 | 55 | 55 | 55 | 50 | 45 | 40 | 35 | 25 |

Below 60°C the crystalline/amorphous ratio seems to be frozen. The specific heat of polythene is greater than that of the pure paraffins, and increases rapidly as the melting point is approached, indicating an increasing amount of disorder in the solid structure which culminates in the disappearance of crystallinity at 115°C. The change of degree of crystallinity with temperature, obtained from *Figure 56*, broadly follows the specific volume results, and indicates that the material is about 75 per cent crystalline at room temperature.

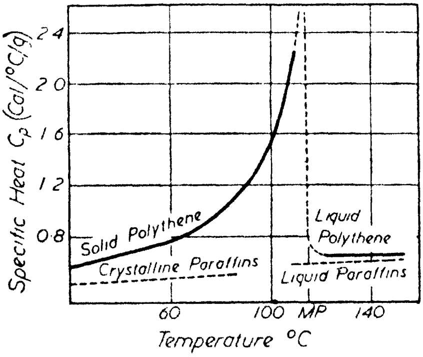


*Figure 56. Specific heat of Polythene*
(*Reference* : 27)

It is well known that rubber, if kept at 0°C or cooled to lower temperatures, becomes hard and inextensible. It is also known that on stretching rubber to its greatest extension it will remain extended. On warming stretched rubber to a definite temperature, a contraction occurs, and in the contracted state it displays the mechanical properties which we associate with rubbers. Many of the synthetic rubbers show the same phenomenon, and X-ray studies have shown that the effect of cooling or stretching is to induce crystallization in the rubber. Measurements of the rate of crystallization of stretched rubber show that the crystals are formed in a matter of seconds at room temperature but, if the sample is maintained in the stretched condition, further crystallization occurs over a period of weeks, or even longer.[28] Crystallization occurs in unstretched rubber on cooling within the range − 50°C to + 15°C. At the lower temperature crystallization is a very slow process, and below − 50°C no crystallization occurs at all. In this respect rubber and other polymers differ markedly from low molecular weight organic molecules. The progress of crystallization on stretching and cooling has been quantitatively examined by X-rays, specific volume, and optical methods. *Figure 57* shows the crystalline/amorphous ratio as a function of the extension at room temperature.[29] TRELOAR [30] estimates that at 0°C the change in volume on crystallization is of the order of 4 per cent and that at least 90 per cent of the fully extended rubber is crystalline.

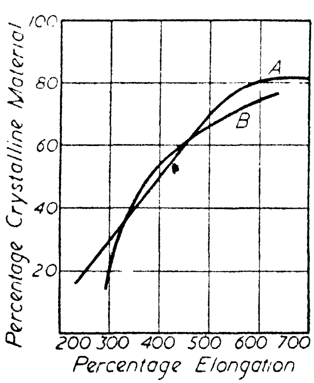


*Figure 57. X-Ray determination of crystalline material: A unvulcanized, B vulcanized, rubber* (*Reference* : 29)

If polyethylene is cooled rapidly from the molten state to room temperature, the solid contains a high proportion of the amorphous phase. The product is, however, still partly crystalline. In fact, neither shock cooling nor any other method has yet been found to give an entirely amorphous product.[27a] The shock cooled polyethylene anneals very quickly on warming. Polyethylene obviously crystallizes very easily, and this is understandable in view of the small size of the repeating unit, which makes it most favourable for orientation. In the substituted polythenes, containing polar or alkyl groups, crystallization is not simply an alinement of the molecules, but requires the arrangement of the units in the correct positions for packing in the crystals. This is a very much more difficult process than in polyethylene, and many polymers on quenching from the melt produce a completely amorphous form, which is stable at room temperature. Others, such as the polyesters, which may be readily produced in the supercooled state in which they are poorly crystalline, anneal and reorientate to crystalline forms at room temperature within a few weeks.[22] In contrast, the polyamides on rapid cooling from the melt give a whole range of partially ordered states depending on the degree of quenching. Unlike polyethylene or the polyesters, the stronger intermolecular forces stabilize the disordered states over long periods of time. The change in orientation in these structures can be observed in the appearance of the x-ray diffraction patterns as a sharpening of the rings or side spacing. This change of orientation with temperature of quenching manifests itself in a remarkable variation of the properties of the solids. The least ordered polyamides are transparent, pliable, and plastic, whilst the highly orientated crystalline structures are opaque, hard, and waxy. These properties are clearly shown in the measurements of FULLER, BAKER and PAPE [31] and are recorded in *Figure 58*, which shows the change of modulus of polyhexamethylene sebacamide samples quenched at various temperatures. Polyvinylidene chloride shows similar properties.[32] The amorphous form obtained on rapid cooling of the fused polymer is soft, rubbery, and capable of mechanical working. This form, however, is not stable, and crystallizes on standing to a hard, tough solid. Complete re-ordering of the chains never occurs in any polymer and there is always an amorphous portion present. This contributes a degree of softening to the structure, and it is these regions which account for the toughness and elastic properties of the apparently rigid polymers. The physical properties of the material greatly depend on the degree of order. The crystalline regions may be regarded as tying together the constituent molecules, and thus leading to increased tensile strength and reducing flow or creep under load. The degree of crystallinity decreases with increase in temperature. The mechanical properties change accordingly, and in a fairly well defined temperature range the disorder becomes so

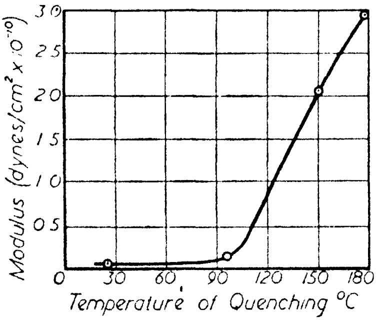


*Figure 58. Hardness of polyamide quenched at various temperatures* (*Reference* : 31)

great that the material takes on rubber-like characteristics. In a few cases, such as cellulose, in which the material exists in a highly crystalline state and the intermolecular forces are very strong, chemical decomposition occurs before the rubbery state is reached.

*Mechanism of Crystallization*—The process of the gradual transition from the amorphous to the partly crystalline state can be understood if we follow the change from the molten to the supercooled state. The liquid consists of long chain molecules randomly distributed and of irregular and rapidly changing configurations, resulting from the free rotation around single bonds. In spite of this apparent randomness, experimental observation shows that sections of the chains associate in parallel layers. Electron diffraction measurements on polyethylene[33] show clearly the existence of some degree of orientation, even in the liquid. This is confirmed by the observations of UBBELOHDE,[34] who found that the hydrocarbon, octadecane, melted over a range of 10°C on either side of the temperature normally regarded as the melting point. He regarded the abnormally high specific heat in the region of the melting point as the extra heat necessary to disorder the hydrocarbon clusters which remained associated in the liquid. These zones of partial alinement of the molecules may be regarded as the nuclei from which crystallization begins and, on cooling, the intermolecular attraction between the chain segments overcomes the thermal motion of the chains, and crystallization over small lengths occurs. As cooling proceeds, more chains and greater lengths aline and the amorphous content decreases. At a sufficiently low temperature, readjustment and mobility of the chain segments becomes increasingly difficult, and a state is reached in which the structure is apparently stable, but not in true thermodynamic equilibrium. Sudden quenching from the melt will produce a state in which the chains are largely in a completely disorientated state. Attraction between individual pairs or small groups of polar groups will be predominant, and if this attraction is great enough, the chains will remain irregularly orientated. The amorphous state will then be stable over indefinite periods.

Since crystallization nuclei are formed irregularly throughout the mass, it is obvious that the growing nuclei, consisting of parts of long chains, will interfere with each other in such a way that a certain amount of material remains in the disordered state. All portions of the chains can never be fitted into the crystal lattice, and hence some chains will project from the crystalline into the amorphous regions or, more probably, a single chain may form part of two or more crystalline and amorphous zones.

In an unstretched, rubber-like polymer the crystallites are orientated at random. On stretching, the molecules in the amorphous regions are forcibly extended, and further alinement of the chains occurs. The crystallites are now very nearly all parallel to the axis of the specimen, and the amount of crystalline material is greater than in the unstretched specimen. A diagrammatic representation of the unstretched and stretched rubber is shown in *Figure 59*, the parallel bundles of chains representing the crystallites.

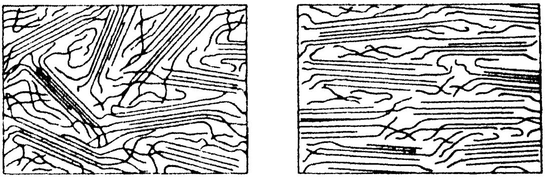

Unstretched Stretched

*Figure 59. Two-dimensional representation of structure of crystalline polymer*

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# CHAPTER 7

# STRUCTURE AND PHYSICAL PROPERTIES OF HIGH POLYMERS

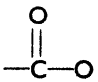
## INTERMOLECULAR FORCES AND CHAIN PACKING

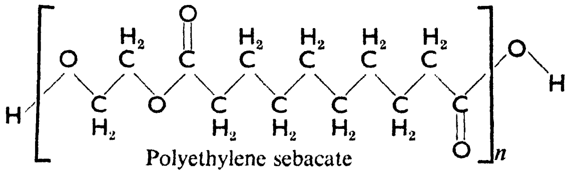
IT IS POSSIBLE to interpret the very wide range of properties shown by linear polymers in terms of two factors: *a* the kind and extent of molecular order or arrangement, and *b* the nature of the packing and the intermolecular forces between the chains. As we have already seen, when the molecular order is high the solid approaches the degree of perfection of a crystal and the repeating units are geometrically arranged in a lattice in three dimensions. At the other extreme, when no order exists, the structure is that of an amorphous solid. A 'crystalline' polymer is, however, never truly crystalline in the sense of a single crystal, but consists of regions of various degrees of order, ranging from the truly crystalline to the amorphous. The extent of the crystallinity and the properties of the solid—whether it is fibrous, plastic, or rubbery—are determined by the characteristics of the configuration and chemical structure of the individual chains. In this chapter we shall consider the detailed relationship between structure and the physical and mechanical properties of particular types of polymer.

*Vinyl Derivatives*—If we take polyethylene as our basic example, then the X-ray evidence shows (Chapter 6) that the molecule has the shape and structure of the long chain paraffin hydrocarbons, and its properties are somewhat similar to those of a crystalline hydrocarbon wax. In the highly ordered form, with the shape of a fully extended zigzag chain, the molecules pack together like parallel rods of dumbbell cross section.[1] The forces holding the chains together are the van der Waal dispersion forces between the methylene ($CH_2$) groups of neighbouring molecules. These forces are relatively weak and fall off rapidly with distance. The structure therefore favours glide planes, across which the forces are weak. The relatively soft, waxy nature and low melting point of polyethylene support these conclusions. If the hydrogen atoms of the $CH_2$ groups are substituted by hydrocarbon groups in a regular manner, as in polyisobutene or polystyrene, the ease with which the chains pack together is greatly reduced. Thus, polyisobutene is like rubber at room temperature and shows extensibility up to fifteen times its original length; in addition, it has no wax-like properties. The stretched form is, however, highly crystalline. The detailed structure of the molecule has not yet been worked out, but the close packing of the methyl groups not only reduces the van der Waal forces between the chains, but also confers great molecular flexibility on the structure.

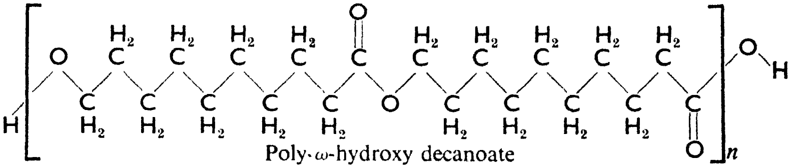
The resemblance to the paraffinic chain structure is almost completely destroyed by the substitution of large groups such as the phenyl in polystyrene. Polystyrene is like glass and non-crystalline even when stretched, and gives only diffuse x-ray patterns. It may be that the side groups are irregularly placed stereochemically along the chains, and so prevent the molecules forming crystalline arrangements.

Substitution of alternate methylene groups of the main paraffin chain by a polar side group (polyvinyl alcohol, chloride, acetate, *etc*) or by two side groups (polyvinylidene chloride, polymethyl methacrylate, *etc*) produces a new type of chain interaction. The polarity of the substituent greatly increases the attraction between the chains, and the range of the forces is increased since, whereas the dispersion forces decrease as $1/r^6$, the dipole forces vary only as $1/r^3$, where $r$ is the distance between the centres of attraction. The structures and properties of this type of polymer will be determined primarily by the relation between chain composition and packing. For small highly polar substituents, such as Cl or CN groups, the dipole–dipole interaction becomes the dominant influence on chain packing. Just as polyethylene provides the extreme example of the non-polar interaction, the systems of polyvinyl chloride, polyvinylidene chloride, and polyacrylonitrile are the extremes of polar concentration. These polymers are tough and brittle. In the case of acrylonitrile, interaction is so high that the polymer is almost infusible and insoluble except in the most highly polar solvents. The strong CN group interaction in the chain may be reduced by the substitution of the hydrogen atom of the $>$CHCN group by the non-polar methyl group which shields the dipoles from interaction. A much softer product of m.p. 115°C, which is readily soluble, is formed.[2] A similar effect is obtained with the highly polar vinyl compounds by copolymerization. For example, the copolymer of acrylonitrile and butadiene has rubber-like properties.

*Polyesters and Polyamides*—In the polyesters the  $-\overset{\overset{\displaystyle O}{\|}}{C}-O$ group is inserted into the paraffin chain at regular and controlled intervals, determined by the dibasic acid and the glycol used in their formation. Some typical chains are the following



Polyethylene sebacate

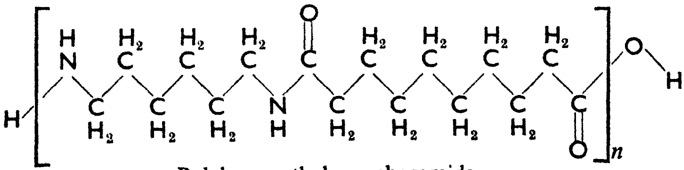


Poly-ω-hydroxy decanoate

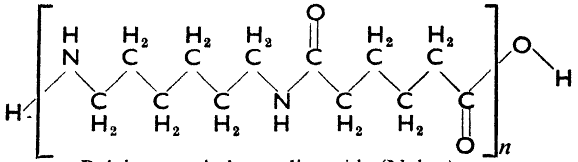
The dipolar linkages may be spaced by an odd or an even number of methylene spacers. The introduction of polar groups into the paraffin chain has a material effect on the properties, and the polyesters are harder and tougher than polythene, owing to the stronger interaction forces of the dipoles.

As we have already seen in the previous chapter, x-ray study shows that the dipoles of the polyesters coordinate in sheets. The exact way in which this happens depends on the chemical composition of the chain. For example in the even ester, poly-ω-hydroxy undecanoate, the dipoles are all on one side of the chain, whereas in the odd ester, poly-ω-hydroxy decanoate, the dipoles alternate from side to side of the planar configuration. The best coordination occurs when the dipole layers are normal to the axis, and less close packing results when these layers are tilted, as in the even members.[3]

By the introduction of NH or OH groups into the hydrocarbon chain, as in the polyamides, the interchain forces are enormously increased by the formation of the comparatively strong hydrogen bonds between the CO and NH groups of adjacent chains. The following diagram shows the composition of two typical polyamides. Like the polyesters, the higher members are paraffin-like and are modified only by the insertion of the polar group.



Polyhexamethylene sebacamide



Polyhexamethylene adipamide (Nylon)

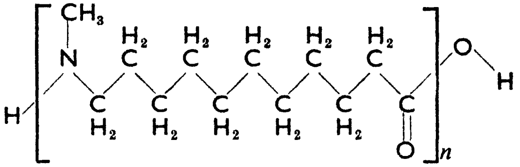
In these regular molecules the spacing of the polar groups does not greatly alter the zigzag carbon chain, which remains essentially as in polyethylene. The molecules coordinate in sheets in two dimensions by hydrogen bond formation,[2] as shown in *Figure 53*.

## CHAIN DILUTION AND COPOLYMERIZATION

As the number of dipole groups in the paraffin chain increases, the dipole–dipole interaction becomes more and more important. The trend in properties follows the increase in intermolecular force, and polymers in which the interaction is high become high melting, insoluble, hard and brittle. The properties may be modified by reduction of the polar interaction, or by copolymerization. The former effect has already been mentioned in the polyamide or polyester series, where chemical methods of preparation are adopted to control the dilution of the relative ‘ soft ’ methylene groups between the strongly interacting polar groups. In the vinyl series the substitution of the hydrogen by alkyl or aryl groups has a modifying effect, but with this class of polymers another and important method of achieving a decrease in intermolecular action and at the same time a reduction in the ease of chain packing is by the introduction of base units of different sizes. This is achieved by copolymerization, and is familiar in the vinyl copolymers and the synthetic rubbers. Copolymerization introduces units which destroy the regularity of the chains, and hence the tendency to pack together in the crystalline form. Other effects of copolymerization which are related to crystallinity are reduced softening temperature and increased solubility in organic solvents.

In the copolyamides made from ω-amino acids of different lengths and from mixed dibasic acids and mixed diamines the attraction centres are shifted up or down from the coordination layers along the chain axis. This explains the softening and increased extensibility of these copolymers compared with the parent ‘ single ’ polymer systems.[3]

In hydrogen bonded chain molecules the forces may be greatly reduced without upsetting the regularity by substitution of the hydrogen atom involved in the bonding by an alkyl group. Thus, in the polymer formed by the self-condensation of ω-methylamino-undecanoic acid



the structure is considerably loosened and the solid is more flexible and softer than the corresponding ω-amino-undecanoic acid polymer, which is a hard, tough solid. The substituted product is soluble in weakly polar solvents such as chloroform, whereas the unmethylated polymer is soluble only in strong hydrogen bond forming solvents like *meta*-cresol. The effect of the degree of methylation in the N-methylated polyamides has been investigated in detail by BAKER and FULLER.[5] As the methyl substitution in a representative member of the series—polydecamethylene sebacamide—increases from 0 to 55 per cent, the physical properties show a gradual change from a hard and brittle to a rubber-like solid. The elastic modulus and hardness decrease rapidly with increasing N-methylation, due to the decrease in the hydrogen bonding. At the same time the relative solubility in weakly polar solvents increases. *Figures 60* and *61* illustrate these results. An X-ray examination of the

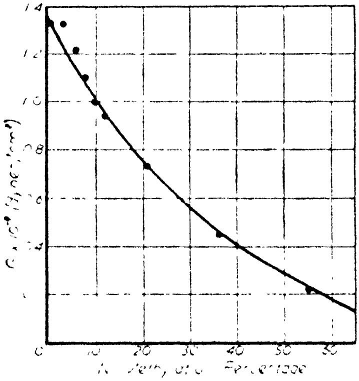


*Figure 60. Dependence of Young's modulus G on the molar proportions of N-methylation for polydecamethylene sebacamides*

(*Reference* : 5)

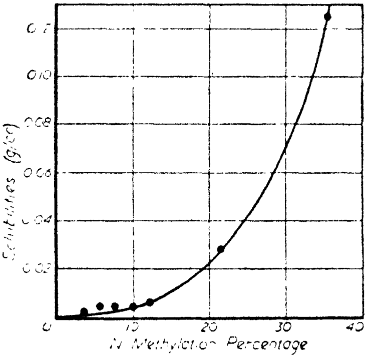


*Figure 61. The relative solubilities in ethanol/chloroform mixture of polydisperse samples of polydecamethylene sebacamides of comparable molecular weights*

(*Reference* : 5)

polymers showed that the interchain spacing of 4·4 Å, characteristic of hydrocarbon chains, was not appreciably affected by the methyl substitution, and that the chains pack as in a pure hydrocarbon. The spacing between the dipole layers, related to the identity period, is more than 25 per cent shorter in the crystal of the lower methylated product than that corresponding to the fully extended chain. The retraction of the chains is explained as a partial folding along the fibre axis (*q.v.*). The retracted spacing can be converted into the extended form by stretching. *Figure 62* shows the change in fibre period caused by stretching an annealed retracted fibre. The retraction is reduced on weakening the polar interaction, and the polymers become more amorphous and rubbery. The X-ray pattern of the products, when more than half of the dipolar linkages had been replaced by methyl groups, emphasized the lateral disorder, and the polymers are the most rubbery of the series.

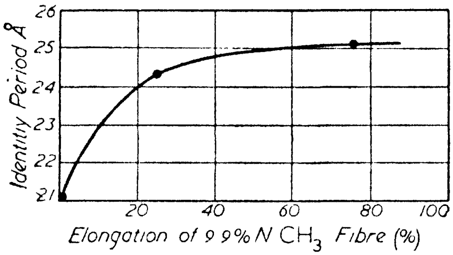


*Figure 62. Change in identity period caused by stretching fibre of* 9·9% N CH$_3$ *polydecamethylene sebacamide*

(*Reference* : 5)

The following mechanism was proposed by Baker and Fuller [5] to explain the observed retraction and may represent the first stage in rubbery elasticity. The association of the polar groups at the end of each hydrocarbon chain, which does not favour hydrocarbon packing, arises by a twisting of these groups. There is thus a competition between the paraffinic portion and the associated dipole portion of the chain. As a consequence, at each dipole layer there is a torque tending to skew portions of the chains from the paraffinic into the polar arrangement, and the result is a rotation about the free bonds near the polar linkages and so the chains progress as shown in *Figure 63*. A sufficiently high concentration of polar groups yields a structure dominated by polar coordination, and thus the extended configuration of *Figure 63* is obtained.

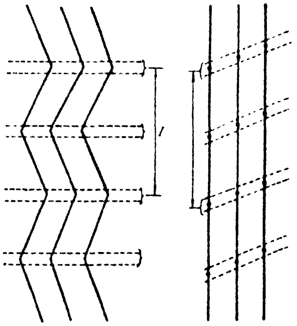
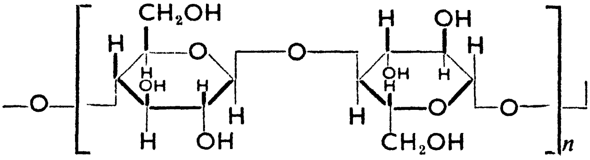


*Figure 63. Possible scheme of chain unkinking accompanying elongation of substituted polyamides and other rubber-like materials*

(*Reference* : 5)

*Cellulose Derivatives*—The principles of polar coordination, chain packing, and modification of properties by substitution apply, in general, to cellulose and its derivatives and other complex molecules. It is immediately apparent from an examination of the open chain structure of cellulose



that the high relative fraction of hydroxyl groups may participate in hydrogen bonding and that the forces holding the chains together are very strong. Furthermore, the structure reveals pronounced steric hindrance around the oxygen bridge and a very limited amount of rotation and flexibility of the units relative to one another. Cellulose has a very high melting point, and does not flow on heating. Substitution of the hydroxyl groups gives derivatives which may be solidified from the molten state to produce either crystalline or amorphous structures. For example, cellulose triacetate shows a high degree of crystallinity when solidified near its fusion point, but a highly amorphous state when quenched at a low temperature. The two forms exhibit widely different mechanical properties, the crystalline modification being the harder and stronger. The x-ray patterns indicate that in the quenched state the chains are locally parallel but randomly orientated around the fibre axis. At temperatures below the melting point the chains have sufficient kinetic energy to permit resumption of the ordered state. This chain rearrangement occurs at a much lower temperature in the tributyrate than in the triacetate and, since the groups are of similar polar nature, this effect must be due to the larger size of the acyl groups, which tend to force the chains farther apart. In the mixed ester, cellulose acetate-butyrate, in which substitution of the three hydroxyl groups is not complete and hydrogen bonding is still possible, we have the combination of both the above effects—high intermolecular action due to hydrogen bonding and chain separation by the large substituent. In this case the form obtained on slowly cooling is highly crystalline, but the quenched state is highly amorphous. On account of the strong polar forces, the quenched form is stable over long periods, and does not anneal to the crystalline state below the melting point.

## PLASTICIZATION

The action of large substituents in the cellulose molecule discussed above, in loosening the structure by forcing the chains apart with a consequent softening of the solid, may be regarded as an internal plasticization by the ester groups. The preceding ideas of chain packing suggest that the weakening of the polar interaction by solvation should produce similar configuration changes to those caused by substitution or dilution by weakly interacting groups. If the solvating agent disorders the polymer entirely, then solution occurs. The specific polar groups in the polymer may, however, be solvated without the development of extensive disorder in other parts of the same chains. BAKER and FULLER[5] have shown that, when an annealed polymethylene sebacamide is exposed to cresol vapour or other hydrogen bond forming substances, the cresol forms bonds at the polar groups and disorders the polar planes. This weakening of the polar forces without a serious disruption of the paraffin packing seems to provide a clear picture of the mechanism of plasticization. Water, a typical hydrogen bonding solvent, has a similar effect with the cellulose esters and permits increased chain motion.

In the general problem of plasticizer action three types of intermolecular forces exist: those between polymer molecules, those between plasticizer molecules, and those between plasticizer and polymer molecules. A systematic study of the nature of these interactions is necessary to obtain a complete understanding of the plasticizer action. The viscosities of polymer solutions in the plasticizer are influenced by polymer association and polymer/solvent interaction, and we have already seen (page 168) how these measurements provide a comparative measure of plasticizer compatibility. As a result of these interactions, the plasticizer/polymer system exists as a continuous phase and though it is not yet possible to give a quantitative representation of the facts, the qualitative picture is that the solvent type plasticizer functions by loosening the structure, thus conferring greater mobility on the chains and increasing their ease of movement.

## MELTING OF CRYSTALLINE POLYMERS

‘Crystalline’ high polymers, unlike lower molecular weight substances, do not melt at a definite temperature, but melting occurs over a range of temperature. This is undoubtedly due to imperfection of the crystallinity. No ‘crystalline’ polymer is wholly crystalline and, as we have already seen in the last section, a part of the material is always present in the amorphous state. The melting behaviour of the simplest structure, polyethylene, differs from that of the normal saturated hydrocarbons in two ways: *a* the change from the ordered state to the disordered amorphous state occurs over a wide range of temperature, as shown by density (*Figure 55*), specific heat (*Figure 56*) and by optical and x-ray measurements; *b* the melting point for a chain of 1,000 $CH_2$ units is about 20° lower than that predicted from the well established relationship for the melting points $T_F$ of the lower chain paraffins with increase in molecular weight. GARNER, VAN BIBBER, and KING [7] have shown that $T_F$ is given by

$$T_F = \frac{0{\cdot}6085n - 1{\cdot}75}{0{\cdot}001491n + 0{\cdot}00404}$$

where $n$ is the number of methylene units. MEYER and VAN DER WIJK [8] represent the data by the formula

$$\frac{1}{T_F} = 2{\cdot}395 \times 10^{-3} + \frac{1{\cdot}71 \times 10^3}{n}$$

According to these formulae, the melting point of polyethylene when $n = 1{,}000$ should be 134°C and 141°C respectively, compared with the experimental value of 115°C. In order to understand the melting of high polymers, it is necessary to explain these two general facts. It is now believed that the explanation lies in the fact that the chains do not fit perfectly into the crystal lattice, but pass through or project into amorphous regions. ALFREY and MARK,[9] and TRELOAR [10] have discussed the behaviour of such chains. As successive segments of a randomly kinked molecule become attached to the crystallite, both the distance $l$ between the ends of the amorphous segment and the number of links $n_l$ in an amorphous region decrease, but $l$ decreases more rapidly than $n_l$. The randomness is related to the entropy, and thus the entropy of fusion does not decrease linearly with $n_l$. The heat of fusion $\Delta H$ is a linear function of $n_l$, and thermodynamically the melting point, $T_m$, is given by

$$T_m = \Delta H / \Delta S$$

The entropy change on crystallization is different for the different portions of the chain entering the crystallite. This variation in entropy change would then produce a corresponding variation in melting temperature, and hence a melting range. This conception also explains the well known observation that when rubber is crystallized for a long time the tension in the amorphous portion relaxes owing to the slow thermal molecular rearrangement. The amount of the amorphous component is reduced, and thus the melting point rises with long periods of crystallization. Furthermore, since the entropy change in the formation of large crystallites is different from that for small ones, the variable range of crystallite size would be expected to give variable melting point ranges.

The foregoing qualitative ideas have recently been expressed quantitatively by FRITH and TUCKETT.[11] Using as an idealized model an assembly of long chains in which the amorphous fraction ($\theta$) separates the crystalline regions ($1 - \theta$), they show that the free energy, $G$, of the system is a non-linear function of the proportion of the amorphous material—that is, the melting point of the crystalline polymer depends on the proportion $\theta$ of the amorphous material in the structure. By considering the equilibrium state between the crystalline and amorphous phases at any temperature—*i.e.* $\frac{dG}{d\theta} = 0$—it is shown that

$$\frac{n_l l_F}{RT_m} = n_l \cdot \frac{Z - 1}{e} + \frac{1}{\theta} \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

where $n_l$ = number of links between crystal nuclei
$l_F$ = latent heat of fusion per single link
$Z$ = coordination of the lattice
$T_m$ = melting point

The expression contains two molecular parameters, $Z$ and $n_l$, and one experimental quantity, $l_F$. The value of $n_l$ cannot be deduced from chain length measurements and must be partly guessed. The formula is very sensitive to $Z$, and values of the melting points of crystalline rubber and polythene in close agreement with experiment are obtained for $Z$ values of 5·4 and 7 respectively. Using this value of $Z$, the calculated crystalline/amorphous ratio is in surprisingly good agreement with the experimental data of RICHARDS (page 201).

Frith and Tuckett [11] considered only the case of very long unbranched chains. A normal polymer consists of a wide range of molecular sizes, and RICHARDS [12] has recently extended the theory to linear paraffins containing a proportion of short chains which are assumed to be concentrated in the amorphous phase. The mathematical expressions obtained are somewhat lengthy, and reduce to equation (1) when the concentration of the low molecular weight material is negligible. The theoretical expressions are in good agreement with the observed data on the depression of the melting point of polythene by added hydrocarbons.

These theories show that a melting range is a consequence of the coexistence of the amorphous and crystalline phases at any temperature. Such a melting range would occur even if the crystallites were of the same size. However, in the normal crystalline polymer a range of crystallite sizes exists and, on heating, the smallest crystallites containing the shortest chains are most likely to disappear first, the largest persisting with little change until the highest temperatures are reached. The result is that the proportion of amorphous material increases with rise in temperature.

## KINETIC THEORY OF RUBBER ELASTICITY

The fundamental requirement for rubber-like elasticity is a high degree of molecular flexibility. This condition appears in long chain structures when free or nearly free rotation of the atoms or groups occurs around the single bonds forming the chain. The flexibility will be influenced by the nature of the mutual interaction of the individual chains and, as a consequence, it is more likely that rubber-like properties will be observed in systems which have weak secondary forces between the molecules. When the forces are strong, the elastic properties appear only at temperatures which are sufficiently high to loosen and disorder the structure. A third structural detail of importance is the establishment of the interlocking of the units at a few places along the chain. This is necessary because when the chains are under tension they must be sufficiently firmly locked together to form a continuous structure. This is ensured in the vulcanization of rubber by the formation of sulphur cross linkages. Even in unvulcanized rubber, interconnections exist, owing to the complex interaction of the randomly distributed chains.

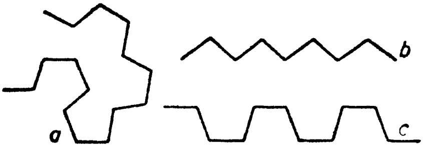


*Figure 64. Irregularly kinked molecule, a ; stretching favours chain configuration b or c*

The basic concept of all explanations of rubber-like properties is the tendency of the chain-like molecules, as a result of their intramolecular thermal motion, to assumed curled up shapes as illustrated diagrammatically in *Figure 64*. Each possible configuration of the molecule corresponds to a definite distance between the ends of the chain (displacement length), which is very much smaller than the length of the extended chain. Since from the point of view of ' free rotation ' a large number of configurations are equally probable, the result must be expressed as a length distribution of the chain. These distributions have been discussed previously in Chapter 4.

The relationship forming the common basis of all the statistical theories of the stress/strain relationship for rubber-like substances, and for random chains, may be expressed in the following way. If one end of the chain is taken as the origin of the coordinates, then the probability that the other end lies within a volume element located at $x$, $y$, $z$ is expressed by

$$p(x,y,z)dxdydz = \beta^3/\pi^{3/2} \,.\, e^{-\beta^2(x^2+y^2+z^2)}dx\,dy\,dz \quad . \quad (2)$$

where the parameter $\beta$ is defined by the equation $\beta^{\frac{1}{2}} = \frac{2}{3}l_c^2Z\dfrac{1+\cos\theta}{1-\cos\theta}$ $l_c$ being the C—C bond distance, $Z$ the number of links in the chain and $180 - \theta$ the valence angle. The dependence of $\beta$ on the flexibility and length of the chain will not alter the form of equation (2), which is the important factor in elasticity theory.

The kinked and coiled configurations are the most likely and so, when a macromolecule is extended, it must tend to contract owing to the thermal motion of its links. This thermal motion can thus be thought of as a tension along the straight line joining the ends of the chain. As the temperature is increased, the thermal motion will be more violent and the tension will be less. This conception of an isolated macromolecular chain exhibiting intramolecular Brownian motion provides a qualitative picture of rubber elasticity. In extending the idea to bulk rubber it is necessary to devise a model of the material. The simplest of these models is that in which a network is formed by the occasional linking together of parts of different molecules, so that over the greater part of their length the intramolecular motion of the molecules is hardly affected (*Figure 65*). The distribution of chain displacement lengths can thus be assumed to conform to that of long chains, [equation (2)]. The different theories of elasticity which have been formulated differ in the type of the network structure assumed and in the derivation of the molecular displacement lengths.

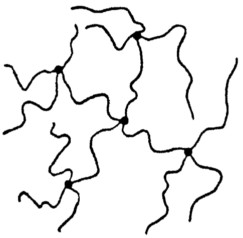


*Figure 65. Diagrammatic representation of network structure of rubber*

Since an elongated chain represents a lower entropy or less probable state than an irregular random configuration, the origin of the retractive force is the tendency of the rubber molecule to form a more probable (disorientated) state. This explanation, due initially to MEYER, VON SUSICH, and VALKO,[13] and subsequently developed mathematically by KUHN [14] and GUTH and MARK [15] is now universally accepted. The problem of calculating the entropy is essentially one of statistical thermodynamics, and involves the calculation of the relative number of configurations as a function of deformation.

If we extend a piece of rubber, the work done against the tension $F$, in order to increase the effective length from $l$ to $l + dl$, is equal to the increase in free energy $G$ at constant temperature. The force $F$ can be defined according to the formula

$$F = \left(\frac{\delta G}{\delta l}\right)_T$$

Now, the assumption of free rotation of the chain links (under conditions of constant values for their lengths and valency angles) is equivalent to the thermodynamic condition that the internal energy of the molecule $U$ is independent of its length. Therefore since $G = U - TS$, where $S$ is the entropy of the macromolecule, it follows that

$$F = -T\left(\frac{\delta S}{\delta l}\right)_T . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

This conclusion has been amply confirmed by the careful experimental studies of MEYER and FERRI.[16]

The thermodynamic equations relating the entropy $S$ and internal energy $U$ with the tension $F$ and length $l$ of the rubber [17] are

$$F = \left(\frac{\delta U}{\delta l}\right)_T - T\left(\frac{\delta S}{\delta l}\right)_T . \quad . \quad . \quad . \quad . \quad (4)$$

$$= \left(\frac{\delta U}{\delta l}\right)_T + T\left(\frac{\delta F}{\delta T}\right)_l . \quad . \quad . \quad . \quad . \quad (5)$$

These equations are analogous to the familiar equations for a gaseous system in which pressure $P$ and volume $V$ are replaced by $-F$ and $l$ respectively. The values of $\left(\frac{\delta U}{\delta l}\right)_T$ and $\left(\frac{\delta S}{\delta l}\right)_T$ may be calculated from measurements of the tension and its temperature variation at constant length. MEYER and FERRI,[16] working up to 350 per cent elongation with vulcanized rubber, showed that the relation

$$F = bT \ (b = \text{constant})$$

was true over a wide range of temperatures. It follows directly from equation (5) that $\left(\frac{\delta U}{\delta l}\right)_T = 0$. This work provided a direct experimental proof of the applicability of the kinetic statistical theory to rubber. Other work substantiates this conclusion. The results of WIEGAND and SNYDER [17] on vulcanized rubber, evaluated by TRELOAR,[18] are shown in *Table XXVII*. Up to extensions of about 350 per cent there is only a small positive energy change on stretching, and the larger part of the tension is due to a decrease of entropy. At higher elongations crystallization begins, as shown by the change of sign of $(\delta U/\delta l)_T$ and the rapid increase of all values. This confirms that the high elastic deformation of rubber is primarily an entropy effect. The theoretical calculation of the elastic tension $F$ thus resolves itself into the evaluation of the entropy change due to the extension.

*Table XXVII*

*Internal Energy and Entropy Changes on Stretching*

| *Extension per cent* | *Tension (gwt)* | $(\delta U/\delta l)_T$ *(gwt)* | $T\left(\frac{\delta S}{\delta l}\right)_T$ *(gwt)* |
|---|---|---|---|
| 158 | 70 | + 20 | − 50 |
| 288 | 104 | + 24 | − 80 |
| 376 | 121 | + 5 | −116 |
| 462 | 113 | −142 | −255 |
| 548 | 131 | −240 | −371 |
| 632 | 156 | −170 | −326 |
| 718 | 250 | +390 | +140 |

We can now briefly review these theories, which are usually based on the following assumptions:

*1* The $N$ molecules of the network all have the same chain length
*2* The distribution of lengths (*i.e.* displacement lengths) of the molecules in the unstretched state are those given by Kuhn's statistical formula, equation (2)
*3* On extension, the components of length of the individual molecules are changed in the same ratio as the corresponding dimension of the bulk rubber
*4* Deformation takes place without change of volume.

Assumption *4*, initially used by KUHN [14] and WALL,[19] is shown above as an established experimental fact.

Equation (2) gives the probability $p$ of a chain having components of length between $x$ and $x + dx$, $y$ and $y + dy$, and $z$ and $z + dz$, and the entropy of a single chain can then be determined from the Boltzmann relationship, $s = k \ln p$. $s$ is given by $[A - \beta^2(x^2 + y^2 + z^2)]$, where $A$ is a constant. The contribution to the total entropy per cc due to molecules of the above length components is obtained by multiplying the entropy $s$ by the appropriate number of molecules. Integration gives the total entropy $S$, corresponding to the unstretched state. For the stretched state, corresponding to an extension in the $x$ direction by a fractional amount $\gamma = \left(\frac{l}{l_0} - 1\right)$, the distribution of molecular length is

$$p'(x,y,z)dx\,dy\,dz = \frac{\beta^3}{\pi^{3/2}} \cdot e^{-\beta^2\left[\frac{x^2}{(1+\gamma)^2} + (y^2 + z^2)(1+\gamma)\right]} dxdydz. \quad . \quad (6)$$

and the total entropy $S'$ in the stretched state is obtained by using equation (6) instead of equation (2). Evaluation of the integrals [14] leads to the approximate relation

$$S' - S = -3/2Nk\gamma^2$$

and from equation (3) the linear stress/strain relation is

$$F = 3NkT\gamma$$

This result is approximate, since in its derivation powers of $\gamma$ higher than $\gamma^2$ were neglected. If this is avoided, then, as shown by TRELOAR,[21] the accurate form of the stress/strain relationship is not linear but is given by

$$F = NkT\left(\alpha - \frac{1}{\alpha^2}\right)$$

where $\alpha = (1 + \gamma)$ is employed to represent the ratio of the lengths in the $x$ direction before and after extension.

A similar result was deduced by WALL,[19] employing the same distribution relationships, but an entirely different mathematical procedure. In his treatment, Wall renounced the plan of calculating the entropies of individual chains, but considered the probabilities of the stressed and unstressed states in their entirety. The tension $F$ (force per unit initial cross sectional area) is given by either of the alternative expressions

$$F = NkT\left(\alpha - \frac{1}{\alpha^2}\right) = \frac{\rho RT}{\overline{m}_n}\left(\alpha - \frac{1}{\alpha^2}\right) \cdot \quad . \quad . \quad (7)$$

where $\rho$ is the density and $\overline{m}_n$ the molecular weight per chain (number average)—that is, between junction points in the network. In using this equation it is important to bear in mind that the original statistical treatment of Kuhn, upon which these developments were based, assumed that the displacement length was small compared with that of the unstretched chain. The formulae cannot, therefore, be expected to apply to the whole of the stress/strain curve of rubber. The experimental work has confirmed that the theoretical equations are in reasonably good agreement with experimental data at small or moderate strains, but not at large strains [21] (*Figure 66*). In order to extend the theory over the whole range of possible strains, it is necessary to use a more accurate distribution function. This has been carried out by TRELOAR,[21] and the theoretical curves show the essential features of the corresponding experimental curves for natural rubber right up to the breaking point, though the extensibility of real rubber is less than the theoretical. This development was made possible by the use of an alternative treatment of the rubber network deformation proposed by FLORY and REHNER.[22] Instead of considering the chains as individual elements, four chains are considered as radiating from each point of the cross linkage, the position of the end of each of these four chains being at the corners of a regular tetrahedron. A deformation of the rubber produces a corresponding deformation of the elementary tetrahedron. This model is shown in *Figure 67*. The point *P* represents the junction, and the four chains are shown as wavy lines. The probability that the central junction lies in a volume element *P* will depend on the product of four probability functions of the type given by equation (2). This probability decreases with distance of *P* from the centre of the tetrahedron *O*. On integrating throughout space, the probability of the undeformed network was obtained. Upon repeating the calculation for the deformed tetrahedron, and comparing with the above, the entropy per cross link was found to be

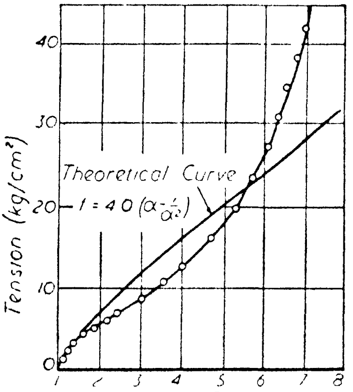


*Figure 66. Extension in one direction for rubber* (8% *sulphur*) *at* 20°C (*Reference* : 20*b*)

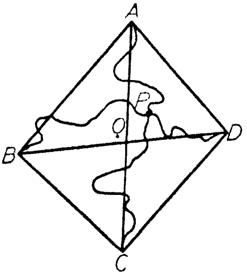


*Figure 67. Unit tetrahedral 'cell' surrounding the central junction P* (*Reference* : 22)

$$S = k\left(\alpha^2 + \frac{2}{\alpha} - 3\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)\cdot$$

where $k$ is the Boltzmann constant. Multiplying by the number $\left(\frac{N}{2}\right)$ of cross linkages leads to previously derived equations for the entropy of deformation of the bulk rubber. The identical result obtained by widely different procedures is reassuring.

Another method of approach to the calculation of the properties of a network has been developed by GUTH and JAMES.[23] They consider cured soft rubber as consisting of a network of flexible chains linked together by sufficient cross bonds to give the material a permanent structure without suppressing the internal Brownian movement of the molecular chains. As we have already seen, flexible chains exert strong retractive forces, but this tendency of close packing is counteracted by the steric forces acting in the opposite direction in the elements of the network. In their theory Guth and James picture this opposing force as an outward push due to an outward pressure of a fictitious incompressible fluid through which the network of chain molecules extends. Under equilibrium conditions the inward pull due to the contracting tendency of the network is balanced by the outward push of the pressure of the liquid. An external force is represented by an outward pull and from a treatment of the equilibrium condition for a simplified network consisting of three independent sets of molecular chains running along the $x$, $y$, $z$ forces of a parallelepiped they deduce the stress/strain relationship

$$F = KT\left(\alpha - \frac{1}{\alpha^2}\right)$$

where $K$ is a constant which may be related to molecular magnitudes. This equation is precisely of the same form as that deduced by other methods which treat the actual network.

### ELASTICITY AND FLOW IN HIGH POLYMERS[24]

Rubber-like materials are unique in their ability to undergo large reversible deformations under the application of relatively small stresses. The molecular mechanism responsible for this high elasticity, as we have seen, is the rearrangement of the molecular chains. This occurs without any appreciable change in the distance between the molecules and is completely reversible. In contrast, the ordinary elastic deformation of inorganic crystals or of a metal is connected with an increase in the mean distance between the particles. On release of the stress the system returns to its original state.

In the deformation of simple amorphous substances both a reversible and an irreversible deformation may occur. Any deformation which produces a direct rearrangement of the particles is always accompanied by an irreversible displacement or plastic (viscous) flow. In polymers the irreversible displacement is limited by the large dimensions of the molecules. Viscous flow requires a rearrangement of the macromolecules (with respect to each other) as a whole, and thus the irreversible deformation is impeded in comparison with that of simple molecules. Under the action of an external force the total elastic deformation comprises three effects, and may be expressed generally as

$$D = D_{OE} + D_{HE} + D_{VISC}$$

where $D_{OE}$ is the ordinary elastic deformation connected with reversible changes in the mean distance between structural elements and is accompanied by a volume change; $D_{HE}$ is the high elastic deformation, and depends on the degree of orientation as determined by the statistical equilibrium between the orientating action in the external field and the disturbing action of the heat motion of the chains. The last term refers to viscous flow.

At low temperatures the orientational rearrangement of the rubber particles occurs very slowly, the high elasticity is suppressed, and deformation occurs principally by ordinary elastic processes with a high Young's Modulus ($\approx$40,000 kg/cm$^2$). At room temperature the observed modulus of high elasticity of rubber is of the order of 20 kg/cm$^2$—that is, about 2,000 times less. This shows that the deformation of rubber at room temperature is connected almost entirely with the rearrangement of the particles. The ordinary elastic deformation of polymers obeys the general laws established for crystalline bodies and metals, and at any temperature the elastic strain changes with time proportionally to the applied force; recovery on removal of the deforming stress is instantaneous. The highly elastic deformation, on the other hand, does not respond immediately to variations in the external force, but lags behind it by an amount dependent upon the mobility of the particles. At every temperature there is a finite probability of rearrangement of particles dependent on the kinetic motion. The time taken for this rearrangement to occur is called the orientation time,[27, 28] and will be larger at low temperatures. Obviously in a polymer consisting of many different sizes of molecules, there will be a whole range of orientation times. The rate of rearrangement is favoured by thermal motion, but hindered by molecular forces, and is therefore strongly temperature dependent.

The general form of the curve of the deformation of an amorphous polymer under constant stress (load) is shown in *Figure 68*. The ordinary elastic deformation is attained at once, but the time-dependent component is complex and consists of chain uncoiling and viscous flow. When the load is removed the deformation is slowly reduced and the specimen may regain its original dimensions. If, instead of applying a constant stress at zero time a constant deformation is applied, then it is found that a gradual decrease or relaxation of load takes place during the time under strain, as shown in *Figure 69*.

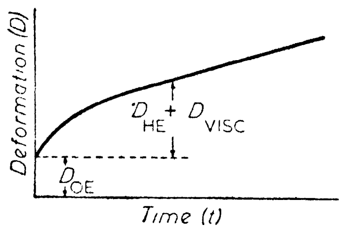


*Figure 68. Deformation/time curve for constant stress*

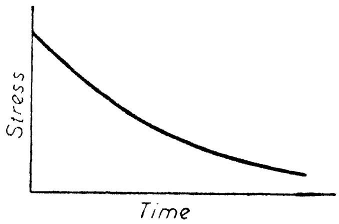


*Figure 69. Showing relaxation of stress under constant deformation*

Expressing this concept in quantitative terms, the probability $p$ that a particle rearranges from one state to another requires the overcoming of a potential barrier of height $\mu$, and is given by $p = C \,.\, e^{-\mu/kT}$, where $C$ is a constant, $k$ the Boltzmann constant and $T$ the absolute temperature. The rate of rearrangement is inversely proportional to $p$ and thus the orientation time $\tau$ may be expressed as

$$\tau = A \,.\, e^{\mu/kT} \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Therefore, assuming that the deformation takes place under a constant force

$$D_{HE}(t) = D_{HE}(\infty)\,(1 - e^{-t/\tau}) \quad . \quad . \quad . \quad (10)$$

where $t$ = time from the moment of the application of stress, $D_{HE}(t)$ is the component of highly elastic deformation at this time, and $D_{HE}(\infty)$ is the final equilibrium value of $D_{HE}(t)$. Thus the total elastic deformation of the substance as a function of temperature and time may be written

$$\begin{aligned} D_{(t,\tau)} &= D_{OE} + D_{HE}(t) \\ &= D_{OE} + D_{HE}(\infty)(1 - e^{-t/\tau}) \\ &= D_{OE} + D_{HE}(\infty)\left(1 - \exp \frac{-t}{Ae^{\mu/RT}}\right) \\ &= D_{OE} + D_{HE}(\infty)t/Ae^{\mu/RT} \text{ for } t/\tau < 10^{-1}. \quad . \quad (11) \end{aligned}$$

If viscous flow is included, there is an additional term, $t\tau/\eta$, where $\eta$ is the viscosity. $D_{OE}$ is usually so very much smaller than either $D_{EL}$ or $D_{VISC}$ that it can be neglected. In rubber, $\tau$ is very small at room temperature, $D_{HE}(\infty)$ being reached almost at once, and so it is unnecessary to consider the time dependence of $D_{HE}$ in the ordinary kinetic theory of rubber.

If the duration of the applied stress is very short compared with the orientation time, there will be insufficient time for orientation to occur, ' highly elastic ' deformation will not be established, and the polymer will behave as a rigid solid. Thus, short durations of stress, such as occur with periodic stresses of high frequency at low temperature, accentuate solid-like characteristics; longer stress times (or low frequencies), and higher temperatures promote high elasticity or rubber-like behaviour. *Figure 70* shows the results of ALEXANDROW and LAZURKIN[26] for vulcanized rubber. The change of frequency from 1 to 1,000 vibrations per minute at room temperature leads to a variation of the modulus of elasticity of rubber of 10 per cent, while at −40°C a similar change in frequency results in a tenfold variation of the modulus. The experimental curves for these and other polymers are in close qualitative agreement with theory. It appears, therefore, that the dependence of the deformation of highly elastic bodies on temperature is determined by the ratio of the time of orientation to the frequency of the applied force.

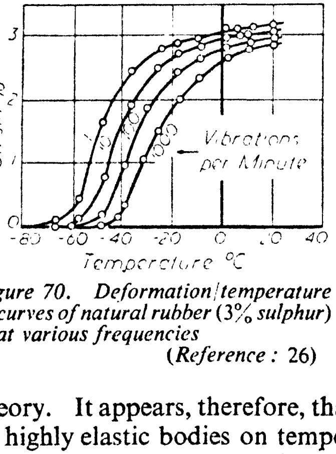


*Figure 70. Deformation/temperature curves of natural rubber* (3% *sulphur*) *at various frequencies*
(*Reference :* 26)

The relationship (9) may be expressed as $\tau = Ae^{\Delta H_{EL}/RT}$, where $\Delta H_{EL}$, the activation energy, may include contributions from both elastic and viscous flow. This law is obeyed for a number of polymers, the plot of log $\tau$ against $\frac{1}{T}$ giving good straight lines, over a small temperature range, from which $\Delta H_{EL}$ can be evaluated. Treating the phenomenon as a rate process, we may write the full rate equation

$$k' = \frac{kT}{h} \cdot e^{-\Delta G^*_{EL}/RT} = \frac{kT}{h} \cdot e^{\Delta S^*_{EL}/R} \cdot e^{-\Delta H^*_{EL}/RT} \quad . \quad . \quad (12)$$

where $k' = \frac{1}{\tau}$ and $\Delta G^*_{EL}$, $\Delta H^*_{EL}$, and $\Delta S^*_{EL}$ are the Gibbs free energy, heat content change and entropy of activation respectively. Using the data of *Figure 70*, ELEY [27] obtained the values listed in *Table XXVIII*. The Gibbs free energy term determines the orientation time—the characteristic quantity describing the time behaviour at any temperature. As Eley has pointed out, the distinction between rubber-like materials and an amorphous polymer like methacrylate is determined by the free energy of activation, $\Delta G^*_{EL}$, and since the entropy differences play a small rôle, the main distinction is associated with the heat of activation, $\Delta H^*_{EL}$, for the orientation of the chains. This is determined by the intermolecular forces between the chains and the development of free rotation around the C—C bonds of the chain. It is to be expected in agreement with the results of *Table XXVIII* that polymethyl methacrylate, having a higher lateral cohesion than rubber, will only develop elasticity at a higher temperature. The data also show that plasticizers which decrease chain interaction lower the temperature at which elasticity develops; cross linking of rubber raises this temperature.

*Table XXVIII*

| | $\Delta H^*_{EL}$ kcal mol$^{-1}$ | $\Delta S^*_{EL}$ kcal mol$^{-1}$ | $\Delta G^*_{EL}$ kcal mol$^{-1}$ |
|---|---|---|---|
| *Natural rubber + 3% S* | 38 | 104 | 7 |
| *Chloroprene* | 38 | 99 | 8·5 |
| *Partly vulcanized ebonite* | 55 | 121 | 19 |
| *Polymethyl methacrylate + 30% plasticizer* | 52 | 87 | 26 |
| *Polymethyl methacrylate + 10% plasticizer* | 59 | 95 | 31 |
| *Polymethyl methacrylate without plasticizer* | 75 | 122 | 39 |

Referring to equation (11), it is seen that the relative magnitudes of $t$ and $\tau$ determine whether a given polymer exhibits high elasticity at a given temperature. If $\tau \gg t$, $D_{HE}$ hardly develops at all, and $D_{OE} \gg D_{HE(t)}$. In general, owing to the relatively small values of $\Delta H^*_{EL}$, there will be no sharp demarcation between the two regions of high elasticity (low Young's Modulus) and the ordinary energy elasticity (high Young's Modulus). In comparing the elastic properties of different polymers, TUCKETT [28] has defined an elastic temperature $T_E$ at which $\tau$ has a fixed value (say 1 sec). If $T_E$ (corresponding to a $\tau$ value comparable with the average time of loading) is much less than room temperature, then the polymer under normal conditions can undergo large reversible extensions. *Table XXIX* gives some approximate values of $T_E$ for a number of unplasticized polymers. $T_E$, according to this definition, is essentially dependent on $\tau$, and hence on $\Delta G^*_{EL}$. Since $\tau$ increases with decrease in temperature, a situation would ultimately be reached in which the equilibrium value of high elastic strain would not be established for all practical purposes.

*Table XXIX*

| *Polymer unit* | $T_E$ °C |
|---|---|
| *Isoprene (rubber)* | − 50 to − 70 |
| *Chloroprene* | − 50 to − 70 |
| *Isobutene* | − 50 to − 70 |
| *Vinyl acetate* | + 35 to + 45 |
| *Methyl methacrylate* | + 70 to + 90 |
| *Styrene* | + 70 to + 90 |
| *Vinyl chloride* | +100 to +110 |

When rubber or polyisobutene is cooled to a low, but definite and characteristic temperature, a change occurs from the normal state to a form which has been likened to the ‘ glassy state ’. With rubbers this corresponds to a change in physical properties from their normal state of toughness and high elasticity to a brittle and inextensible material. The transition is accompanied by other changes in physical properties. In the region of the temperature of transition there is a rapid—almost continuous—increase in the heat capacity and the thermal coefficient of expansion. In contrast to the fusion of a solid, no latent heat effect or sudden increase in volume occurs. This type of phenomenon is termed by EHRENFEST ‘ a transition of the second order ’, since discontinuities occur, not in the heat content and volume of the substance, but in the temperature derivatives of these quantities. Second-order transitions have been observed at fairly well defined temperatures in the the case of all high polymeric substances which have been studied.[28] Thus the transition temperature is a point of reference below which all rubber-like materials lose the properties of high elasticity and above which any polymeric material acquires rubber-like properties. *Table XXX* summarizes the transition temperatures for a number of high polymers ranging from − 74°C for polyisobutene to 80°C for polystyrene. The transition temperatures are very variable and dependent to some extent on factors such as the rate of heating, plasticizer content, molecular weight, *etc.* The second-order transitions are not phase changes in the thermodynamic sense, and there seems to be general agreement that at the transition temperature the chains lose the property of freedom of molecular rotation, and

*Table XXX*

*Second-order Transition for High Polymers*

| *Material* | $T_m$ °C |
|---|---|
| *Polyisobutene* | —74 |
| *Natural rubber* | —73 |
| *Polyvinyl chloride* | —75 |
| *Polyvinylidene chloride* | —17 |
| *Polystyrene* | 80 |

become fixed as in a glass. This change in molecular motion does not occur at a fixed temperature, as in a first-order transition (melting), but over a temperature range. Since high elasticity is associated with comparatively free rotation which develops at different temperatures for individual polymers, it is reasonable to identify the ' second-order transition temperature ', $T_m$, as revealed by diverse physical measurements, with $T_E$ values for a fixed (but unknown) $\tau$ value.

The second-order transition temperature has also been identified with the so-called ' brittle point '.[28, 29] This property is derived from measurements of mechanical properties, and is the temperature below which the polymer specimen breaks on the sudden application of a load without preliminary stretching; above the brittle point temperature, elastic and viscous flow occur before fracture. The brittle point cannot be specified completely. The nature of the brittle point test is such that the result depends on the manner of carrying out the test, but in terms of the above picture the change at the brittle point is the same as the onset of highly elastic deformation and therefore corresponds to $T_E$ for a small relative strain.

## ELECTRICAL PROPERTIES OF HIGH POLYMERS[30]

Apart from the interest in the electrical properties of polymers arising from their wide use as insulators, the study of these properties provides a valuable method of investigation of the structure of polymers and the relation between chemical structure and mechanical properties. In contrast to the method of study of mechanical properties, in which a deformation is applied to the outside of a matrix of molecules and the resultant effect on the individual molecules is assessed indirectly, the application of an electric field to a polar polymer may be regarded as a direct application of a constraint to the molecules themselves. The process of dipole orientation in the electric field is controlled by relaxation times and activation energies, and it is of interest to compare these results with the analogous processes involved in viscous and elastic deformations.

In terms of the Debye theory of the properties of polar liquids, the dielectric constant is a consequence of the presence of dipoles in these materials. When a constant electric field is applied to the dielectric it is polarized almost immediately by the displacement of the electrons of the atoms with respect to their nuclei. This gives rise to an electron displacement current which is present for all frequencies and in all substances. It corresponds to the limiting value of the dielectric constant at high frequencies, and is numerically equal to the square of the refractive index. In the hydrocarbon polymers such as polyethylene, polyisobutene, polystyrene and rubber, the dielectric constant will approach the optical value, and will be independent of frequency and temperature. The higher dielectric constant of polar substances arises from the additional polarization resulting from the orientation of the dipoles in the direction of the applied field. In the absence of the field, the distribution of the dipoles is uniform, but in a D.C. field each molecule tends to swing parallel to the field and to produce a component of polarization in the direction of the field. This polarization is opposed by the thermal motion of the molecules, and the alinement will not be perfect. On removal of the field the orientation does not disappear instantaneously, and the molecules take a finite time to return to their random distribution. The rate of return will depend on the viscous properties of the medium and on the temperature. The time $\tau$ for the average orientation to drop to one $e$th of its steady state value is called the electrical relaxation time. When the period of the field is long compared with the time of relaxation, the equilibrium orientation will be established in a single cycle. We then have a polarization in phase with the field, and the system shows its maximum dielectric constant, $\varepsilon_0$.

Some idea of the factors which determine the magnitude of $\tau$ can be obtained if we regard the dipoles as spheres of radius $a$ immersed in a continuous medium of internal viscosity, $\eta$. The rate of return of the molecules to their normal distribution will be slower the more viscous the liquid, and faster the higher the temperature. Thus, we may write

$$\tau \sim \eta a^3/T$$

The experimental results show that $\eta$ cannot be identified with the macroscopic viscosity.[31]

If, instead of a D.C. field, we apply an A.C. field, the molecules will tend to oscillate towards one electrode and then the other in order to follow the field. If the frequency is increased, a condition is reached when the orientation lags behind the reversal of the field, and at very high frequencies the molecules will not follow the field at all. Thus, polar molecules exhibit high dielectric constants at low frequencies and low dielectric constants at high frequencies. On account of this decrease of dipole orientation with increasing frequency, the dielectric constant will decrease from the maximum value $\varepsilon_0$. As the frequency increases the orientation lags more and more behind the reversals of the field and thus the polarization will be out of phase with the field. This phase difference $\delta$ is the loss angle of the dielectric and tan $\delta$ the power factor. The phase lag gives rise to a heat dissipation in the dielectric which is proportional to tan $\delta$ and the frequency $\omega$. These properties are generally expressed in terms of a complex dielectric constant $\varepsilon$, which is usually split into its real and imaginary components, the experimental constant $\varepsilon'$ and the loss factor $\varepsilon''$ respectively. It may be shown [30] that

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + \omega^2\tau^2} \quad . \quad . \quad . \quad . \quad . \qquad (13)$$

$$\varepsilon'' = \frac{(\varepsilon_0 - \varepsilon_\infty)\omega\tau}{1 - \omega^2\tau^2} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (14)$$

where $\varepsilon_\infty$ is the atomic polarization and $\omega = 2\pi \times$ frequency. The loss factor measures the electrical energy converted into heat, and will be a maximum when the period of the field just matches the relaxation time of the molecule. The curve of $\varepsilon''$ against $f$ thus goes through a maximum when $2\pi f\tau = 1$ ($f$ = frequency), whilst that of the dielectric constant $\varepsilon'$ follows an S-shaped curve with $\varepsilon_0$ and $\varepsilon_\infty$ as asymptotic values.

When we apply this theory, derived for simple polar molecules, to the experimental results with polar polymers, it accounts only qualitatively for the observations. With increase in temperature the dielectric constant increases from a low value to a limiting value independent of frequency [32] (*Figure 71*), and the loss factor goes through a maximum at the frequency $f_{max} = \frac{1}{2\pi\tau}$ (*Figure 72*). These similarities indicate that linear polymers behave like liquids of high viscosity, and that the electric response is due to dipole orientation. This viewpoint is supported by much independent evidence. However, in spite of this qualitative similarity with polar liquids, it has long been known that equations (13) and (14) do not fit the facts very exactly. Several important discrepancies occur, the most striking of which are in the shapes of the $\varepsilon'$ and

$\varepsilon''$/frequency curves. In the absorption region the change of dielectric constant with frequency is much less than required by equation (13); secondly, according to the Debye theory, the height of the maximum should exactly equal $\frac{1}{2}(\varepsilon_0 - \varepsilon_\infty)$, but in general, with polymers $\varepsilon''$ (max) is less than this, and the high losses extend over a much wider band of frequencies than is given by equation (14). Furthermore, different polymers give differently shaped curves. The explanation of these differences lies in the fact that for the simple polar liquid to which the Debye theory applies, the molecules are all of one type; the dipoles are the same, and can thus be treated as independent molecules. In the polymer the dipoles are coupled in a long chain, and it is inconceivable that the whole polymer molecule can orientate as a unit. On account of the flexibility of the chain, the molecule can assume many different configurations, determined by the orientation of its segments. Each of these segments can be regarded as a unit to which may be assigned a relaxation time. The polymeric chains thus behave like a mixture of molecules, each with a different $\tau$, and to each of which there corresponds an independent $\varepsilon'$ or $\varepsilon''/\log f$ curve. The net effect may be regarded as the superposition of these separate curves, and this accounts for the broadening and shape of the dispersion curve. It is necessary, therefore, to consider a relaxation time distribution for the high polymeric system. This has been discussed by many investigators, and an approximate distribution has been calculated

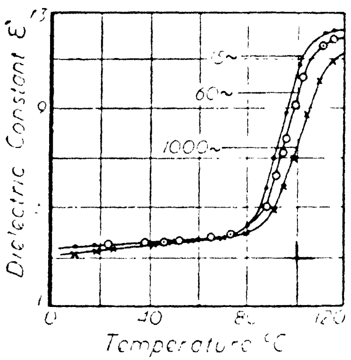


*Figure 71. Effect of temperature on the dielectric constant of polyvinyl chloride at frequencies* 15, 60, *and* 1,000 *cycles/sec*

(*Reference :* 32)

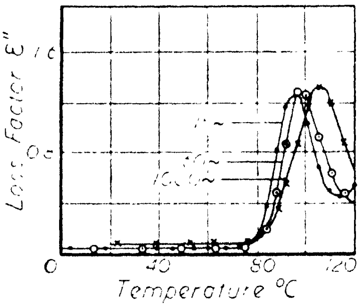


*Figure 72. Effect of temperature on the loss factor of polyvinyl chloride at frequencies* 15, 60, *and* 1,000 *cycles/sec*

(*Reference :* 32)

theoretically by FUOSS and KIRKWOOD,[33] who deduced the empirical equation

$$\varepsilon'' = \varepsilon' \tan \delta = A(\operatorname{sech} \alpha \log f_{max}/f)$$

where $\alpha$ is a parameter which determines the breadth of the distribution curve at half height. The value of $\alpha$ is unity for a single relaxation time, but becomes smaller and approaches zero as the spread of relaxation times increases. This equation has been found to fit the observed loss factor/frequency curves approximately. Fuoss and Kirkwood observed that in a series of plasticized polyvinyl chloride samples the value of $\alpha$ decreased as the plasticizer content decreased at constant temperature—that is, as the sample became more and more rigid. A similar effect is shown in the chlorinated polythenes [34] as the chlorine content is increased, the increase in $\tau$ (average) being in accord with the change from a flexible or rubbery to the rigid state.

The spread of relaxation times may also be expected if there are more than one type of dipole present, as in a copolymer, or if the dipoles are irregularly arranged along the chain, as in chlorinated polythene.

The comparatively high dielectric constants of polar polymers is a further consequence of molecular structure. For instance, the dielectric constant of polyvinyl chloride is about 2½ times that of ethyl chloride. In the polar liquid composed of small molecules the rotation of the molecules is strongly influenced by their different fields, and they associate together with cancellation of their moments. Mutual compensation is much less probable in polar polymers, in spite of the high molecular flexibility, and only occurs with rare configurations. For this reason we expect higher static dielectric constants in polar polymers than in the corresponding monomers.

## ELECTRICAL AND MECHANICAL ORIENTATION TIMES

Investigations of the mechanical and electrical properties of polymers have shown that orientation of sections of the molecular chain occurs on the one hand during high elastic deformation and, on the other hand, under the influence of an applied electric stress. Both are rate processes characterized by orientation times. Increased intermolecular forces, brought about, for example, by an increase in polar group concentration, decrease the flexibility, but increase both the mechanical ($\tau_{HE}$) and electrical ($\tau_{DO}$) orientation times. From a consideration of the temperature dependence of these processes, TUCKETT [35] has shown that the activation energies of dipole orientation and the activation energy for elastic flow are similar. The temperature variation of the time of relaxation is given by $\tau = Ae^{-E_{DO}/RT}$, where $A$ may be regarded as independent of temperature and $E_{DO}$ = activation energy for dipole orientation. $E_{DO}$ can be calculated approximately from the change with temperature of the average orientation time $\tau_{DO}$, which is given approximately by $\tau_{DO} = \frac{1}{2\pi f_{max}}$. With vinyl acetate the plots of log $f_{max}$ against the reciprocal of the absolute temperature give a good straight line corresponding to an activation energy of 57 kcal.[36] The corresponding value for the activation energy for elastic deformation suggests $E = 50\text{–}80$ kcal, which is in agreement with the electrical data. Close correspondence is also found in other polymers which, like vinyl acetate, have dipoles in the main chain; but in others, such as methyl methacrylate, new effects appear which may be attributed to rotation of side groups alone. This marked similarity in the activation processes for mechanical and electrical orientation indicates that the same molecular process is involved in both sets of phenomena. This connection is clearly brought out by a further consideration of the molecular mechanism.[35]

If we consider a linear polymer with $n$ polar repeating units, then each unit will have a dipole moment $\mu_i$ and any chain will have a resultant dipole moment, $\sum_i^n \mu_i$. Just as there is a most probable distance between the ends of a chain, so there is a most probable resultant dipole moment. In an electric field denoted by a vector $F$, the resultant moment in the direction of $F$ is $(F\mu_i)_{average}$. Any resultant moment different from the most probable would correspond to another configuration. For polymers in which the C—X dipole is part of the main chain, this configurational change must involve rotations around the C—C bonds, and hence is similar to elastic deformation. The attainment of less probable configurations is governed by intermolecular forces in each case, and thus both electrical and elastic orientation times evaluate the same properties.

The correlation may be taken a stage farther. The temperature at which a flexible polymer changes on cooling to a rigid state (second-order transition) has been identified with the temperature at which the high elastic orientation time, $\tau_{HE}$, reaches a value of a second or so, that is, a value comparable with the time of the duration of a typical brittle or softening point test. This change in mechanical properties has been shown by MEAD and FUOSS [37] to correspond to a sudden and very marked decrease in $\varepsilon'$ and $\varepsilon''$. This is in general agreement with the conclusion that at the second-order transition point, rotational freedom of the chains is frozen.

If $\tau_{HE} \sim \tau_{DO}$, there should be a relation between the temperature at which $\tau_{DO} = 1$ sec and the second-order transition temperature. This is clearly shown in the following table, compiled by TUCKETT.[35]

*Table XXXI*

| *Polymer* | *Electrical temp. at which* $\tau_{\infty} = 1$ *sec* | *Mechanical data (qualitative)* |
|---|---|---|
| *Vinyl chloride* . . . | 87°C | *Brittle point* 80°C<br>*Fully elastic at* 115°C |
| *Vinyl acetate* . . . | 44°C | *Brittle point* 35-40°C |
| *Methyl acrylate* . . | 15°C | *Brittle point* ~ 0°C |
| *Methyl methacrylate* . | 20°C | $t = 1$ *sec at* ~ 125°C |

Although the evidence is not conclusive, the results indicate the equivalence of the orientation times. In both processes the time deduced represents the time for a certain rearrangement to take place in the structure. There are, however, other observed orientation times which have no parallel in mechanical properties. Rigid polymers in which $\tau_{HE}$ is greater than 1 sec show power factor maxima at high frequencies. It appears that processes other than rotation of the main chain are involved. Tuckett has emphasized that in making the comparison between elastic and electrical properties, it is essential to choose the correct absorption bands. Thus, methyl methacrylate shows two bands due to dipole rotation caused by movement of the backbone carbon chain and rotation in the side groups alone. The serious disagreement for methyl methacrylate in *Table XXXI* is due to the existence of these two types of orientation, and the results recorded there probably refer to side-chain rotation. The former type of rotation would be expected at higher temperatures.

## APPENDIX

Since this Chapter was written a theory of crystallization of a network structure has been developed by FLORY [*J. chem. Phys.* 15 (1947) 397, 408]. This theory predicts only moderate degrees of crystallinity at crystallization equilibrium. The experimental observation of high crystallinity during the stretching process is attributed to severe departures from the equilibrium condition when crystallization occurs.

The melting point relationship deduced by FRITH and TUCKETT (p. 216) is shown to originate from their implied assumption that the ends of the chains in the amorphous region are free to locate anywhere.

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